

Some Basic Concept of Chemistry

SOME USEFUL CONVERSION FACTORS

$$1 \text{ \AA} = 10^{-10} \text{ m}, 1 \text{ nm} = 10^{-9} \text{ m}$$

$$1 \text{ pm} = 10^{-12} \text{ m}$$

$$1 \text{ litre} = 10^{-3} \text{ m}^3 = 1 \text{ dm}^3$$

$$1 \text{ atm} = 760 \text{ mm or torr}$$
$$= 101325 \text{ Pa or Nm}^{-2}$$

$$1 \text{ bar} = 10^5 \text{ Nm}^{-2} = 10^5 \text{ Pa}$$

$$1 \text{ calorie} = 4.184 \text{ J}$$

$$1 \text{ electron volt(eV)} = 1.6022 \times 10^{-19} \text{ J}$$

$$(1 \text{ J} = 10^7 \text{ ergs})$$

$$(1 \text{ cal} > 1 \text{ J} > 1 \text{ erg} > 1 \text{ eV})$$

ATOMIC MASS OR MOLECULAR MASS

Mass of one atom or molecule in a.m.u.

$$\text{C} \rightarrow 12 \text{ amu}$$

$$\text{NH}_3 \rightarrow 17 \text{ amu}$$

Actual Mass

Mass of one atom or molecule in grams

$$\text{C} \rightarrow 12 \times 1.6 \times 10^{-24} \text{ g}$$

$$\text{CH}_4 \rightarrow 16 \times 1.6 \times 10^{-24} \text{ g}$$

Relative Atomic Mass or Relative Molecular Mass

Mass of one atom or molecule w.r.t. $1/12^{\text{th}}$ or ^{12}C atom

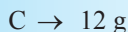
$$\text{C} \rightarrow 12$$

$$\text{CH}_4 \rightarrow 16$$

It is unitless

GRAM ATOMIC MASS OR GRAM MOLECULAR MASS

Mass of one mole of atom or molecule



It is also called molar mass

DEFINITION OF MOLE

One mole is a collection of that many entities as there are number of atoms exactly in 12 gm of C-12 isotope.

The number of atoms present in exactly 12 gm of C-12 isotope is called Avogadro's number [$N_A = 6.022 \times 10^{23}$]

$$\begin{aligned} 1 \text{ u} &= 1 \text{ amu} = (1/12)^{\text{th}} \text{ of mass of 1 atom of C}^{12} = \frac{1 \text{ g}}{N_A} \\ &= 1.66 \times 10^{-24} \text{ g} \end{aligned}$$

For Elements

- 1 g atom = 1 mole of atoms = N_A atoms
- g atomic mass (GAM) = mass of N_A atoms in g

$$\text{Mole of atoms} = \frac{\text{Mass (g)}}{\text{GAM or molar mass}}$$

For Molecule

- 1 g molecule = 1 mole of molecule = N_A molecule
- g molecular mass (GMM) = mass of N_A molecule in g.

$$\text{Mole of molecule} = \frac{\text{Mass (g)}}{\text{GMM or molar mass}}$$

1 Mole of Substance

- Contains 6.022×10^{23} particles
- Weighs as much as molecular mass/ atomic mass/ionic mass in grams
- If it is a gas, one mole occupies a volume of 22.4 L at 1 atm & 273 K or 22.7 L at STP

For Ionic Compounds

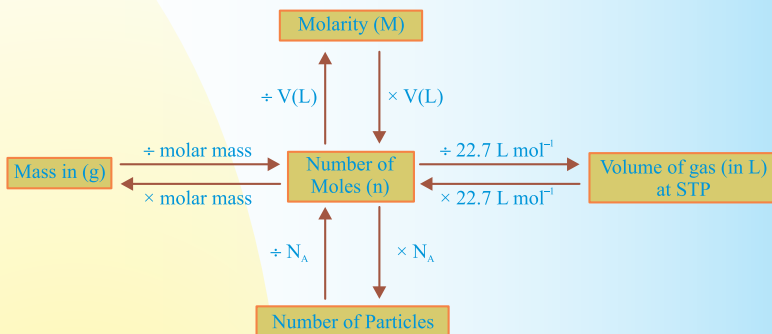
- 1 g formula unit = 1 mole of formula unit = N_A formula unit.
- g formula mass (GFM) = mass of N_A formula unit in g.

$$\text{Mole of formula unit} = \frac{\text{Mass (g)}}{\text{GMM or molar mass}}$$

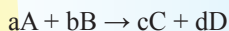
VAPOUR DENSITY

Ratio of density of vapour to the density of hydrogen at similar pressure and temperature.

$$\text{Vapour density} = \frac{\text{Molar mass}}{2}$$



STOICHIOMETRY BASED CONCEPT



- a,b,c,d, represents the ratios of moles, volumes [for gaseous] molecules in which the reactants react or products formed.
- a,b,c,d does not represent the ratio of masses.
- The stoichiometric amount of components may be related as

$$\frac{\text{Moles of A reacted}}{a} = \frac{\text{Moles of B reacted}}{b} = \frac{\text{Moles of C created}}{c} = \frac{\text{Moles of D reacted}}{d}$$

Concept of limiting reagent

If data of more than one reactant is given then first convert all the data into moles then divide the moles of reactants with their respective stoichiometric coefficient. The reactant having minimum ratio will be L.R. then find the moles of product formed or excess reagent left by comparing it with L.R. through stoichiometric concept.

Percentage Purity

The percentage of a specified compound or element in an impure sample may be given as

$$\% \text{purity} = \frac{\text{Actual mass of compound}}{\text{Total mass of sample}} \times 100$$

If impurity is unknown, it is always considered as inert (unreactive) material.

EMPIRICAL AND MOLECULAR FORMULA

- **Empirical formula:** Formula depicting constituent atoms in their simplest ratio.
- **Molecular formula:** Formula depicting actual number of atoms in one molecule of the compound.
- The molecular formula is generally an integral multiple of the empirical formula.

i.e. molecular formula = empirical formula \times n

$$\text{where } n = \frac{\text{molecular formula mass}}{\text{empirical formula mass}}$$

- **For determination of atomic mass:**

Dulong's & Petit's Law:

Atomic weight of metal \times specific heat capacity (cal/gm- $^{\circ}$ C) \approx 6.4.

It should be remembered that this law is an empirical observation and this gives an approximate value of atomic weight. This law gives better result for heavier solid elements, at high temperature conditions.

CONCENTRATION TERMS

| Concentration Type | Mathematical Formula | Concept |
|------------------------|--|--|
| Percentage by mass | $\% \left(\frac{w}{w} \right) = \frac{\text{Mass of solute} \times 100}{\text{Mass of solution}}$ | Mass of solute (in gm) present in 100 gm of solution. |
| Volume percentage | $\% \left(\frac{v}{v} \right) = \frac{\text{Volume of solute} \times 100}{\text{Volume of solution}}$ | Volume of solute (in cm ³) present in 100 cm ³ of solution. |
| Mass-volume percentage | $\% \left(\frac{w}{v} \right) = \frac{\text{Mass of solute} \times 100}{\text{Volume of solution}}$ | Mass of solute (in gm) present in 100 cm ³ of solution. |
| Parts per million | $\text{ppm} = \frac{\text{Mass of solute} \times 10^6}{\text{Mass of solution}}$ | Parts by mass of solute per million parts by mass of the solution |

| Concentration Type | Mathematical Formula | Concept |
|--------------------|---|---|
| Mole fraction | $X_A = \frac{\text{Mole of A}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \dots}$ $X_B = \frac{\text{Mole of B}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \dots}$ | Ratio of number of moles of one component to the total number of moles. |
| Molarity | $M = \frac{\text{Mole of solute}}{\text{Volume of solution (in L)}}$ | Moles of solute in one liter of solution. |
| Molality | $m = \frac{\text{Mole of solute}}{\text{Mass of solvent (Kg)}}$ | Moles of solute in one kg of solvent |

MIXING OF SOLUTIONS

It is based on law of conservation of moles.

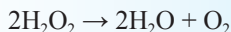
(i) Two solutions having same solute:

$$\text{Final molarity} = \frac{\text{Total moles}}{\text{Total volume}} = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$$

(ii) Dilution Effect: Final molarity, $M_2 = \frac{M_1 V_1}{V_1 + V_2}$

Volume Strenght of H₂O₂ Solutions

Labelled as 'volume H₂O₂' means volume of O₂ (in litre) at 1 bar & 273 K that can be obtained from 1 litre of such a sample when it decomposes according to



- Volume Strenght of H₂O₂ solution = 11.35 × molarity

PERCENTAGE LABELLING OF OLEUM

Labelled as '% oleum' means maximum amount of H₂SO₄ that can be obtained from 100 gm of such oleum (mixture of H₂SO₄ and SO₃) by adding sufficient water. For example, 109% oleum sample means, with the addition of sufficient water to 100 gm oleum sample 109 gm H₂SO₄ is obtained.

% labelling of oleum sample = (100 + x)%

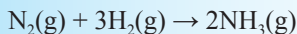
x = mass of H₂O required for the complete conversion of SO₃ in H₂SO₄

- % of free SO₃ in oleum = $\left(\frac{40}{9} \times x\right)\%$

EUDIOMETRY

Some basic assumptions related with calculations are:

1. Gay-Lussac's law of volume combination holds good. According to this law, the volumes of gaseous reactants reacted and the volumes of gaseous products formed, all measured at the same temperature and pressure, bear a simple ratio.

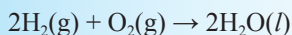


1 vol. 3 vol. 2 vol.

Problem may be solved directly in terms of volume, in place of mole.

The stoichiometric coefficients of a balanced chemical reaction gives the ratio of volumes in which gaseous substances are reacting and products are formed at same temperature and pressure.

2. The volumes of solids or liquids is considered to be negligible in comparison to the volume of gas. It is due to the fact that the volume occupied by any substance in gaseous state is even more than thousand times the volume occupied by the same substance in solid or liquid states.



2 mole 1 mole 2 mole

2 vol. 1 vol. 0 vol.

3. Air is considered as a mixture of oxygen and nitrogen gases only. It is due to the fact that about 99% volume of air is composed of oxygen and nitrogen gases only.
4. Nitrogen gas is considered as a non-reactive gas.
5. The volume of gases produced is often given by certain solvent which absorb contain gases.

| Solvent | Gases absorb |
|---|---|
| KOH | CO ₂ , SO ₂ , Cl ₂ |
| Ammonical Cu ₂ Cl ₂ | CO |
| Turpentine oil | O ₃ |
| Alkaline pyrogallol | O ₂ |
| water | NH ₃ , HCl |
| CuSO ₄ /CaCl ₂ | H ₂ O |



Atomic Structure

IMPORTANT DEFINITIONS

| Proton (m_p)/anode rays | Neutron (m_n) | Electron (m_e) /cathode rays |
|--|----------------------------------|---|
| mass = 1.67×10^{-27} kg | mass = 1.67×10^{-27} kg | mass = 9.1×10^{-31} kg |
| mass = 1.67×10^{-24} g | mass = 1.67×10^{-24} g | mass = 9.1×10^{-28} g |
| mass = 1.00750 amu | mass = 1.00850 amu | mass = 0.000549 amu |
| e/m value is dependent on the nature of gas taken in discharge tube. | | e/m of electron is found to be independent of nature of gas & electrode used. |

REPRESENTATION OF AN ELEMENT



Terms associated with elements:

- Atomic Number (Z): = No. of protons
Electron = Z - C (charge on atom)
- Mass number (A) = Total number of neutron and proton present
A = Number of proton + Number of Neutrons
- **Isotopes:** Same atomic number but different mass number
Example: ${}_6\text{C}^{12}$, ${}_6\text{C}^{13}$, ${}_6\text{C}^{14}$
- **Isobars:** Same mass number but different atomic number
Example: ${}_1\text{H}^3$, ${}_2\text{He}^3$
- **Isodiaphers:** Same difference of number of Neutrons & protons
Example: ${}_5\text{B}^{11}$, ${}_6\text{C}^{13}$

- **Isotones:** Having same number of neutron
Example: ${}_1\text{H}^3$, ${}_2\text{He}^4$
- **Isosters:** They are the molecules which have the same number of atoms & electrons
Example: CO_2 , N_2O
- **Isoelectronic:** Species having same no. of electrons
Example: Cl^- , Ar

ATOMIC MODELS

- **Thomson:** An atom considered to be positively charged sphere where e^- is embedded inside it.
- **Drawback:** Cannot explain stability of an atom.
- **Rutherford Model of an Atoms:**

Electron is revolving around the nucleus in circular path.

$$R_N = R_0(A)^{1/3}, R_0 = 1.33 \times 10^{-13} \text{ cm}$$

[A = mass number, R_N = Radius of nucleus]

SIZE OF NUCLEUS

- The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of 10^{-12} to 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.
- Thus, diameter (size) of the atom is 1,00,000 times the diameter of the nucleus.

ELECTROMAGNETIC SPECTRUM

- $\text{RW} \rightarrow \text{MW} \rightarrow \text{IR} \rightarrow \text{Visible} \rightarrow \text{UV} \rightarrow \text{X-rays} \rightarrow \text{CR}$ (Radiowaves \rightarrow Microwaves \rightarrow Infrared rays \rightarrow Visible rays \rightarrow Ultraviolet rays \rightarrow X-rays \rightarrow Cosmic rays)
- Wavelength decreases \rightarrow
- Frequency increases \rightarrow

$$c = v\lambda \quad \lambda = \frac{c}{v} \quad \bar{\nu} = \frac{1}{\lambda} = \frac{v}{c}$$

$$T = \frac{1}{v} \quad E = \frac{hc}{\lambda} = hv, h = 6.626 \times 10^{-34} \text{ Js}$$

$$E(\text{ev}) = \frac{12400}{\lambda(\text{\AA})}$$

- Total amount of energy transmitted $E = nh\nu = \frac{nhc}{\lambda}$

BOHR'S ATOMIC MODEL

Theory based on quantum theory of radiation and the classical laws of physics

- $\frac{K(Ze)(e)}{r^2} = \frac{mv^2}{r}$
- Electron remains in stationary orbit where it does not radiate its energy.
- **Radius:** $r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$
- **Velocity:** $v = 2.188 \times 10^6 \frac{Z}{n} \text{ ms}^{-1}$
- Energy (KE + PE) = Total energy = $-13.6 \times \frac{Z^2}{n^2} \text{ eV/atom}$
- $TE = -\frac{KZe^2}{2r}$, $PE = \frac{-KZe^2}{r}$, $KE = \frac{KZe^2}{2r}$
 $PE = -2KE$, $KE = -TE$, $PE = 2TE$
- Revolutions per sec = $\frac{v}{2\pi r}$
- Time for one revolution = $\frac{2\pi r}{v}$
- Energy difference between n_1 and n_2 energy level

$$\Delta E = E_{n_2} - E_{n_1} = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \frac{\text{eV}}{\text{atom}} = IE \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where IE = ionization energy of single electron species.

- Ionization energy = $E_\infty - E_{G.S.} = 0 - E_{G.S.}$
 $E_{G.S.}$ = Energy of electron in ground state.

$$E = 21.8 \times 10^{-12} \frac{Z^2}{n^2} \text{ erg per atom}$$

$$= -21.8 \times 10^{-19} \frac{Z^2}{n^2} \text{ per atom}$$

$$= -13.6 \frac{Z^2}{n^2} \text{ eV/atom}$$

$$1 \text{ eV} = 3.83 \times 10^{-23} \text{ kcal}$$

$$1 \text{ eV} = 1.602 \times 10^{-12} \text{ erg}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$E = -313.6 \frac{Z^2}{n^2} \text{ kcal/mole (1 cal = 4.18 J)}$$

$$V = \frac{2\pi kze^2}{nh}$$

$$r = \frac{n^2 h^2}{4\pi^2 m k z e^2}$$

$$E = \frac{2\pi^2 m z^2 e^4 k^2}{n^2 h^2}$$

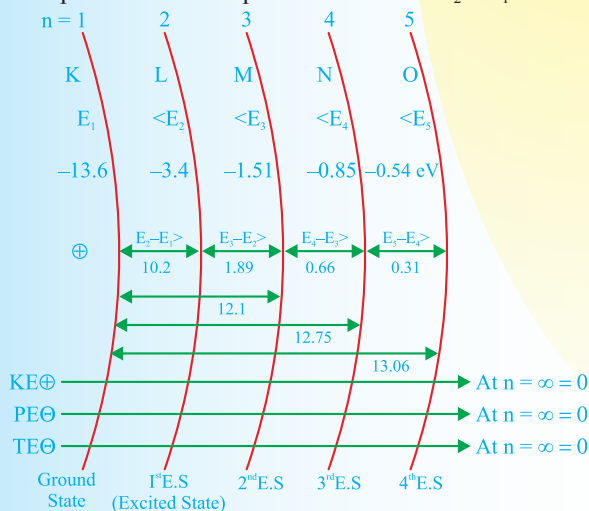
HYDROGEN SPECTRUM

- Rydberg's Equation:**

$$\frac{1}{\lambda} = \bar{\nu} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \times Z^2$$

$R_H \cong 109700 \text{ cm}^{-1}$ = Rydberg constant

- For first line of a series $n_2 = n_1 + 1$
- Limiting spectral line (series limit) means $n_2 = \infty$
- H_α line means $n_2 = n + 1$; also known as line of longest λ , shortest ν , least E
- Similarly H_β line means $n_2 = n_1 + 2$
- When electron de-excites from higher energy level (n) to ground state in atomic sample, then number of spectral lines observed in the spectrum = $\frac{n(n-1)}{2}$
- When electrons de-excites from higher energy level (n_2) to lower energy level (n_1) in atomic sample, then number of spectral line observed in the spectrum = $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$
- No. of spectral lines in a particular series = $n_2 - n_1$.



DE-BROGLIE HYPOTHESIS

- All material particles possess wave character as well as particle character.

- $\lambda = \frac{h}{mv} = \frac{h}{p}$

- The circumference of the n^{th} orbit is equal to n times of wavelength of electron i.e., $2\pi r_n = n\lambda$

Number of waves = n = principal quantum number

- Wavelength of electron (λ) $\cong \sqrt{\frac{150}{V(\text{volts})}} \text{ \AA}$

- $\lambda = \frac{h}{\sqrt{2mKE}}$

HEISENBERG UNCERTAINTY

- According to this principle, "it is impossible to measure simultaneously the position and momentum of a microscopic particle with absolute accuracy"

If one of them is measured with greater accuracy, the other becomes less accurate.

- $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$ or $(\Delta x)(\Delta v) \geq \frac{h}{4\pi m}$

where Δx = Uncertainty in position

Δp = Uncertainty in momentum

Δv = Uncertainty in velocity

m = mass of microscopic particle

- Heisenberg replaced the concept of orbit by that of orbital.

QUANTUM NUMBER

- **Principal Quantum number (By Bohr)**

\Rightarrow Indicates = Size and energy of the orbit, distance of e^- from nucleus

\Rightarrow Values $n = 1, 2, 3, 4, 5 \dots$

\Rightarrow Angular momentum = $n \times \frac{h}{2\pi}$

\Rightarrow Total number of e^- s in an orbit = $2n^2$

\Rightarrow Total number of orbitals in an orbit = n^2

\Rightarrow Total number of subshell in an orbit = n

- **Azimuthal/Secondary/Subsidiary/Angular momentum quantum number (l)**

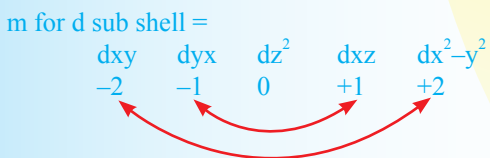
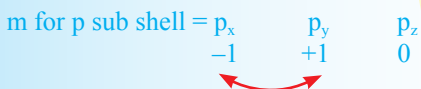
- ⇒ Given by = Sommerfeld
- ⇒ Indicates = Sub shells/sub orbit/sub level
- ⇒ Vales ⇒ 0, 1 ... (n-1)
- ⇒ Indicates shape of orbital/Sub shell

| Value of n | Values of l [Shape] | Initial from word |
|------------|--------------------------------|-------------------|
| eg. | $l = 0$ (s) [Spherical] | Sharp |
| If n = 4 | $l = 1$ [p] [Dumb bell] | Principal |
| | $l = 2$ [d] [Double dumb bell] | Diffused |
| | $l = 3$ [f] [Complex] | Fundamental |

- ⇒ Total no. of e^- s in a suborbit = $2(2l + 1)$
- ⇒ Total no. of orbital in a suborbit = $(2l + 1)$
- ⇒ Orbital angular momentum = $\sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{l(l+1)} \hbar$
 $h = \text{Planck's constant}$
- ⇒ For H & H like species all the subshells of a shell have same energy.
 i.e. $2s = 2p$ $3s = 3p = 3d$

- **Magnetic Quantum number (m)**

- ⇒ Given by Lande
- ⇒ Indicates orientation of orbital i.e. direction of electron density.
- ⇒ Value of $m = -l \dots \dots \dots 0 \dots \dots \dots +l$
- ⇒ Maximum no of e^- s in an orbital = 2
 (with opposite spin)

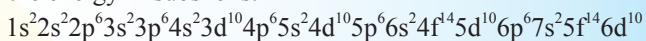


- **Spin Quantum Number (m_s or s)**

- Given by Uhlenback & Goudsmit
- Values of $s = \pm \frac{1}{2}$
- Total value of spin in an atom = $\pm \frac{1}{2} \times \text{number of unpaired electrons}$
- Spin Angular momentum = $\sqrt{s(s+1)} \frac{h}{2\pi}$

RULES FOR FILLING OF ORBITALS

- **Aufbau principle:** The electrons are filled up in increasing order of the energy in subshells.



- **(n + l) rule:** The subshell with lowest (n + l) value is filled up first, but when two or more subshells have same (n + l) value then the subshell with lowest value of n is filled up first.
- **Pauli exclusion principle:** Pauli stated that no two electrons in an atom can have same values of all four quantum numbers.
- **Hund's rule of maximum multiplicity:** Electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electrons with parallel spin.



Gaseous State

GAS LAW

Boyle's law:

$$V \propto \frac{1}{P} (n, T = \text{const}) \quad \boxed{P_1 V_1 = P_2 V_2}$$

Charle's law:

$$V \propto T (n, P = \text{const}) \quad \frac{V_2}{V_1} = \frac{T_2}{T_1}$$

Gay lussac's law:

$$P \propto T (n, V = \text{const}) \quad \frac{P_2}{P_1} = \frac{T_2}{T_1}$$

Avogadro's law:

$V \propto \text{moles} \propto \text{number of molecules} (P, T = \text{const})$

Ideal gas equation $PV = nRT$

$R = 0.0821 \text{ lit atm mol}^{-1} \text{ K}^{-1}$

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ or $8.314, \text{ N}\times\text{m K}^{-1} \text{ mol}^{-1}$

$R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$, $R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$

GRAHAM'S DIFFUSION LAW

It is applicable for non reacting gases

$$r \propto \frac{1}{\sqrt{d}}; r \propto \frac{1}{\sqrt{VD}}; r \propto \frac{1}{\sqrt{M_w}} (P, T = \text{constant})$$

$$VD = \frac{d_{\text{gas}}}{d_{\text{H}_2}} = \frac{M_w}{2}$$

Rate of diffusion

$$r = \frac{l_{\text{diffused gas}}}{t_{\text{time taken}}}; r = \frac{V_{\text{diffused gas}}}{t_{\text{time taken}}}; r = \frac{n_{\text{diffused gas}}}{t_{\text{time taken}}}$$

(When, l = distance traveled by diffused gas)

| Kinetic Gas Equation : $PV = 1/3 nN V_{\text{rms}}^2$ | |
|--|---|
| Dalton's Law of Partial Pressure | Average Kinetic Energy (KE_{av}) |
| $P_{\text{mixture}} = P_1 + P_2 + P_3 \dots (T \& V \text{ const.})$ <p style="text-align: center;"> Partial pressure </p> | $KE_{\text{av}} = \frac{3}{2} nRT \quad (\text{n moles})$ |
| $P_{\text{moist gas}} = P_{\text{dry gas}} + P_{\text{water vapours}}$ | $KE_{\text{av}} = \frac{3}{2} RT \quad (1 \text{ mol or } N_A \text{ molecules})$ |
| <p>It is applicable for non reacting gases.</p> | $KE_{\text{av}} = \frac{3}{2} KT \quad (1 \text{ molecule})$ |
| <p>Methods of determination of partial pressure</p> <p>(P_A & P_B are partial pressure)</p> | $K = 1.38 \times 10^{-23} \text{ JK}^{-1} \text{ molecule}^{-1}$ <p>K is called Boltzman's constant</p> |
| <ul style="list-style-type: none"> From ideal gas equation | $v_{\text{rms}} = \sqrt{\frac{v_1^2 + v_2^2 + \dots + v_n^2}{N}}$ |
| $P_A V = n_A RT \& P_B V = n_B RT$ | $v_{\text{av}} = \frac{v_1 + v_2 + v_3 \dots v_n}{N}$ |
| <ul style="list-style-type: none"> In the form of mole fraction. | $v_{\text{rms}} = \sqrt{\frac{3RT}{Mw}} \quad v_{\text{av}} = \sqrt{\frac{8}{\pi} \frac{RT}{Mw}} \quad v_{\text{mp}} = \sqrt{\frac{2RT}{Mw}}$ |
| $P_A = X_A P_T = \frac{n_A}{n_t} P_T;$ | $v_{\text{rms}} = \sqrt{\frac{3PV}{Mw}} \quad v_{\text{av}} = \sqrt{\frac{8}{\pi} \frac{PV}{Mw}} \quad v_{\text{mp}} = \sqrt{\frac{2PV}{Mw}}$ |
| $P_B = X_B P_T = \frac{n_B}{n_t} P_T \quad [X_A + X_B = 1]$ | $v_{\text{rms}} = \sqrt{\frac{3P}{d}} \quad v_{\text{av}} = \sqrt{\frac{8}{\pi} \frac{P}{d}} \quad v_{\text{mp}} = \sqrt{\frac{2P}{d}}$ |
| $P_T = \text{sum of partial pressure of all gases}$ | $v_{\text{rms}} : v_{\text{av}} : v_{\text{mp}} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2}$ |
| <ul style="list-style-type: none"> In the form of volume fraction. | $= 1 : 0.92 : 0.82$ |
| $P_A = \frac{V_A}{V} P_T \& P_B = \frac{V_B}{V} P_T$ | $v_{\text{mp}} : v_{\text{av}} : v_{\text{rms}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$ |
| <ul style="list-style-type: none"> If individual pressure and individual volume are given | $= 1 : 1.128 : 1.224$ |
| $P_A = \frac{V_A}{V} P_1 \text{ and } P_B = \frac{V_B}{V} P_2$ | <p>Compressibility factor</p> |
| $P_1, P_2 = \text{pressure of gases before mixing}$ | $(z) = \frac{(V_m)_{\text{obs}}}{V_1} = \frac{P(V_m)_{\text{obs}}}{RT}$ |
| $P_A, P_B = \text{pressure of gases after mixing}$ | <p>IF $z = 1$, the gas show ideal gas behaviour. IF $z > 1$, the gas show positive deviation. IF $z < 1$, the gas show negative deviation.</p> |

VANDERWAAL'S EQUATION

Vanderwaal's Equation

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$P_i = P_R + \frac{an^2}{V^2} \Rightarrow P_i > P_R$$

a ↑ force of attraction ↑

liquification ↑;

b ↑ effective size of molecule ↑,

incompressible vol. ↑,

compressible vol. ↓

- At high pressure, Vanderwaal's eqⁿ is

$$\boxed{PV_m - Pb = RT}$$

- At low pressure or Moderate pressure vanderwaal's eqⁿ is

$$\boxed{PV_m + \frac{a}{V_m} = RT}$$

- At very low pressure, high temp. Vanderwaal's Equation is

$$\boxed{VP = nRT}$$

Ideal gas behaviour.

- Gases having ↑ value of a; will have ↑ T_c; ↑ rate of liquefaction.



Thermodynamics

DEFINITION

Deals with interaction of one body with another in terms of energy.

System: Part of universe under investigation.

Surrounding: Rest part of universe except system.

Boundary: Divide system & surrounding

SYSTEM

| Open | Closed | Isolated |
|--------------------------------|--------------------------|---------------------------|
| Energy and matter can exchange | Only energy can exchange | Neither energy nor matter |

| State function | Path function |
|--|---|
| Properties which depends only on initial & final state of system & not on process or path. e.g. U, H, S, G, etc. | Depends on path or process. e.g. work, heat |

THERMODYNAMIC PROPERTIES

| Extensive | Intensive |
|--|---|
| Properties which are dependent of matter (size & mass) present in system | Properties which are independent of matter (size & mass) present in system. |

| Extensive Properties | Intensive Properties |
|---|---|
| Volume Number of moles Mass Free Energy (G) Entropy (S) Enthalpy (H) Internal energy (E & U) heat capacity | Molar volume Density Refractive index Surface tension Viscosity Free energy per mole Specific heat Pressure Temperature Boiling point, freezing point etc. |

PROCESSES

| | | | | |
|--|---|--|--|---|
| Isothermal $T = \text{const.}$ | Isochoric $V = \text{const.}$ | Isobaric $P = \text{const.}$ | Adiabatic No heat exchange $dq = 0$ | Cyclic Initial & final state of system are same |
|--|---|--|--|---|

| Reversible process | Irreversible process |
|--|---|
| <ul style="list-style-type: none"> • Slow process • At any time system and surrounding are in equilibrium. • $P_{\text{sys}} = P_{\text{surr}} \pm dP$ | <ul style="list-style-type: none"> • Fast process • No equilibrium between system and surrounding • $P_{\text{sys}} = P_{\text{surr}} \pm \Delta P$ |

HEAT (q)

Energy exchange due to temperature difference:

$$q = C\Delta T,$$

$$q = nC_m\Delta T,$$

$$q = ms\Delta T$$

C = heat capacity

C_m = molar heat capacity

s = specific heat capacity

m = Amount of substance

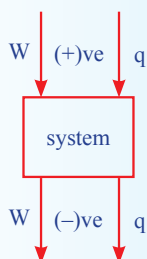
General values of C_V & C_P for an ideal gas can be taken as follows.

| Atomicity | n_{tr} | n_{Rot} | n_{Vib} | C_V | | C_P | | γ | |
|-----------|------------|-----------|-----------|----------------|-----------------|----------------|-----------------|---------------|-----------------|
| | | | | Excl. Vib | Incl. Vib | Excl. Vib | Incl. Vib | Excl. Vib | Incl. Vib |
| Mono | 3 | 0 | 0 | $\frac{3}{2}R$ | $\frac{3}{2}R$ | $\frac{5}{2}R$ | $\frac{5}{2}R$ | $\frac{5}{3}$ | $\frac{5}{3}$ |
| Di | 3 | 2 | 1 | $\frac{5}{2}R$ | $\frac{7}{2}R$ | $\frac{7}{2}R$ | $\frac{9}{2}R$ | $\frac{7}{5}$ | $\frac{9}{7}$ |
| Tri | Linear | 3 | 2 | $\frac{5}{2}R$ | $\frac{13}{2}R$ | $\frac{7}{2}R$ | $\frac{15}{2}R$ | $\frac{7}{5}$ | $\frac{15}{13}$ |
| | Non Linear | 3 | 3 | $3R$ | $6R$ | $4R$ | $7R$ | $\frac{4}{3}$ | $\frac{7}{6}$ |

WORK (W)

| Reversible | Irreversible |
|--|----------------------------------|
| $W_{rev} = -\int_{V_1}^{V_2} P_{ext} \cdot dV$ | $W_{irr} = -P_{ext} (V_2 - V_1)$ |

SIGN CONVENTION



INTERNAL ENERGY (E & U)

Every system having some quantity of matter is associated with a definite amount of energy called internal energy.

$$U = U_{Kinetics} + U_{Potential} + U_{Electronic} + U_{nuclear} + \dots$$

FIRST LAW OF THERMODYNAMICS

Law of conservation of energy

$$\Delta U = q + W$$

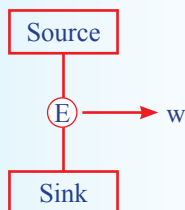
ENTHALPY

$$H = U + PV, \Delta H = \Delta U + (\Delta n_g) RT$$

| Process | Expression for w | Expression for q | Work on PV-graph |
|-------------------------------------|--|--|------------------|
| Reversible isothermal | $w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$ | $q = nRT \ln \left(\frac{V_2}{V_1} \right)$ $q = nRT \ln \left(\frac{P_1}{P_2} \right)$ | |
| Reversible adiabatic process | $w = nC_V(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$ | $q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$ | |

STATEMENTS OF SECOND LAW OF THERMODYNAMICS

- (i) No cyclic engine is possible which take heat from one single source and in a cycle completely convert it into work without producing any change in surrounding.



- (ii) In an irreversible process entropy of universe increases but it remains constant in a reversible process.

$$\Delta S_{\text{syt}} + \Delta S_{\text{sur}} = 0 \quad \text{for rev. process}$$

$$\Delta S_{\text{syt}} + \Delta S_{\text{sur}} > 0 \quad \text{for irrev. process}$$

$$\Delta S_{\text{syt}} + \Delta S_{\text{surr}} \geq 0 \quad (\text{In general})$$

CALCULATION OF ENTROPY CHANGE FOR AN IDEAL GAS

General Expression

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

Reversible & irreversible isothermal expansion or contraction of an ideal gas $\Delta S = nR \ln \frac{V_2}{V_1}$

THIRD LAW OF THERMODYNAMICS

“At absolute zero, the entropy of a perfectly crystalline substance is zero”. which means that at absolute zero every crystalline solid is in a state of perfect order and its entropy should be zero.

VARIATION OF ΔS_r WITH TEMPERATURE & PRESSURE:

$$(\Delta S_r)_{T_2} - (\Delta S_r)_{T_1} = (\Delta C_p)_r \ln \frac{T_2}{T_1}$$

$$(\Delta S_r)_{P_2} - (\Delta S_r)_{P_1} = \Delta n_g R \ln \frac{P_1}{P_2}$$

Similarly

$$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_p)_r (T_2 - T_1) \quad \{\text{Krichoff's equation}\}$$

$$(\Delta U_r)_{T_2} - (\Delta U_r)_{T_1} = (\Delta C_v)_r (T_2 - T_1)$$

GIBBS FREE ENERGY (G) AND SPONTANEITY:

A new thermodynamic state function G, the Gibbs free energy is defined as:

$$G = H - TS$$

at constant temperature and pressure

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

| | | |
|----|------------------------|---|
| If | $(\Delta G)_{T,P} < 0$ | Process is irreversible (spontaneous) |
| | $(\Delta G)_{T,P} = 0$ | Process is reversible |
| | $(\Delta G)_{T,P} > 0$ | Process is impossible (non spontaneous) |

SOME FACTS TO BE REMEMBERED:

(a) Standard condition

- For gases/solid/liquid
P = 1 bar
- For ion/substance in solution
Concentration = 1M

(b) $\Delta G_r = (\Delta G_f)_{\text{product}} - (\Delta G_f)_{\text{reactant}}$

$$\Delta H_r = (\Delta H_f)_{\text{product}} - (\Delta H_f)_{\text{reactant}}$$

$$\Delta S_r = (\Delta S_f)_{\text{product}} - (\Delta S_f)_{\text{reactant}}$$

(All above equation will be derived in thermochemistry)

THERMOCHEMISTRY

BOND ENTHALPY

Average amount of enthalpy required to dissociate one mole gaseous bond into separate gaseous atoms.

$\Delta_r H = (\text{Sum of bond enthalpy of gaseous reactant}) - (\text{Sum of bond enthalpy of gaseous product})$

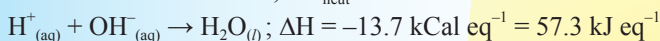
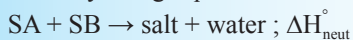
RESONANCE ENERGY

$$\begin{aligned}\Delta H_{\text{resonance}}^{\circ} &= \Delta_f H^{\circ} (\text{experimental}) - \Delta_f H^{\circ} (\text{calculated}) \\ &= \Delta_c H^{\circ} (\text{calculated}) - \Delta_c H^{\circ} (\text{experimental})\end{aligned}$$

ENTHALPY OF NEUTRALIZATION (ΔH_{neut})

(Always exothermic)

Change in enthalpy when one gram equivalent of an acid is completely neutralized by one g-equivalent of a base in dilute solution.



In case of weak acid/base or both $|\Delta H_{\text{N}}^{\circ}| < 13.7 \text{ Kcal/eq}^{-1}$ and the difference is enthalpy of ionisation of ionisation of weak species except in case of HF when $|\Delta H_{\text{N}}| > 13.7 \text{ Kcal/eq}^{-1}$ due to hydration of F^- .



If in a reaction heat of reactant & products are given then heat of that reaction can be measured as follows:

(a) For heat of combustion & for bond enthalpy

$$\Delta_r H = \sum (\Delta H_{\text{C}})_{\text{reactant}} - \sum (\Delta H_{\text{C}})_{\text{product}}$$

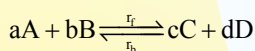
(b) For heat of formation

$$\Delta_r H = \sum (\Delta H_{\text{f}})_{\text{product}} - \sum (\Delta H_{\text{f}})_{\text{reactant}}$$



Chemical Equilibrium

Consider a reversible reaction,



AT EQUILIBRIUM STATE

Rate of forward reaction (r_f) = rate of backward reaction (r_b)

So, at equilibrium,

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{K_f}{K_b}$$

In terms of active mass

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

In terms of partial pressure

$$K_x = \frac{[X_C]^c [X_D]^d}{[X_A]^a [X_B]^b}$$

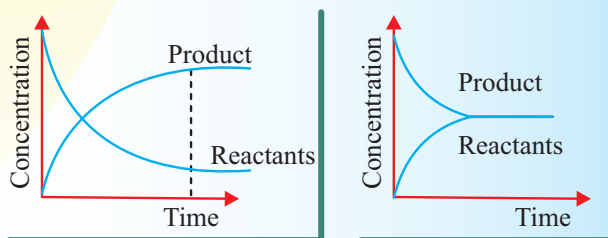
In terms of mole fraction

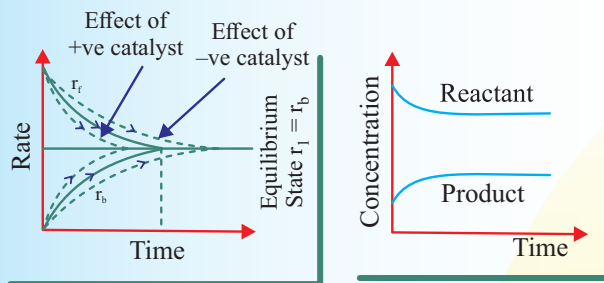
$$K_p = K_C (RT)^{\Delta n_g}$$

While determining Δn_g take only gaseous species.

The active mass of solid & pure liquid is a constant quantity (unity) because it is an intensive property.

GRAPHS





Unit of Equilibrium constant:

$$K_C = (\text{mol L}^{-1})^{\Delta n_g}; K_P = (\text{atm})^{\Delta n_g}$$

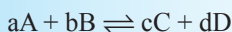
Application of K_C or K_P

- More is the value of K_P or K_C more is the extent of reaction.
- Stability of reactant increases when value of K decreases.
- Stability of Product increases when value of K increase.

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

Predicting the direction of reaction: Reaction Quotient (Q) is expressed in the same way as for equilibrium constant, except that the concentrations may not necessarily be at equilibrium.

In general for the reversible reaction:



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$Q = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \text{ (in terms of pressure)}$$

If $Q = K_{eq}$ then system is in equilibrium

If $Q > K_{eq}$ then system proceed in backward direction to attain equilibrium.

If $Q < K_{eq}$ then system proceed in forward direction to attain equilibrium.

Degree of dissociation (α) $\frac{\text{No. of moles of reactant dissociated}}{\text{No. of mole of reactant present initially}}$

LE-CHATELIER'S PRINCIPLE

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature then the equilibrium is shifted in such a way as to nullify the effect of change.

Le-Chatelier's principle is applicable for both chemical and physical equilibrium.

CHEMICAL EQUILIBRIUM

| Effect due to change in | | $\Delta n_g = 0$ $A \rightleftharpoons B$ | $\Delta n_g > 0$ $A \rightleftharpoons 2B$ | $\Delta n_g < 0$ $2A \rightleftharpoons B$ |
|-------------------------|-------------------------------|--|---|---|
| Concentration | (i) $\uparrow [A]$ | Forward direction | Forward direction | Forward direction |
| | (ii) $\downarrow [A]$ | Backward direction | Backward direction | Backward direction |
| Pressure | (i) \uparrow in pressure | Unchanged | Backward direction | Forward direction |
| | (ii) \downarrow in pressure | Unchanged | Forward direction | Backward direction |
| Temperature | (i) \uparrow in Endothermic | Forward direction | Forward direction | Forward direction |
| | (ii) \uparrow in Exothermic | Backward direction | Backward direction | Backward direction |
| Dissociation | (i) \uparrow in pressure | Unchanged | Dissociation Decreases | Dissociation Increases |
| | (ii) \uparrow in volume | Unchanged | Dissociation Increases | Dissociation Decreases |
| Mixing of inert gas | (i) at constant P | Unchanged | Dissociation Increases | Dissociation Decreases |
| | (ii) at constant V | Unchanged | Unchanged | Unchanged |

Relationship between Equilibrium Constant K , Reaction Quotient Q and Gibbs Energy G

$\Delta G = \Delta G^\circ + RT \ln Q$... (i) where, ΔG° = Standard free energy difference between the products and reactant, T = Absolute temperature in kelvin, R = Universal gas constant.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$, then equation (i) becomes

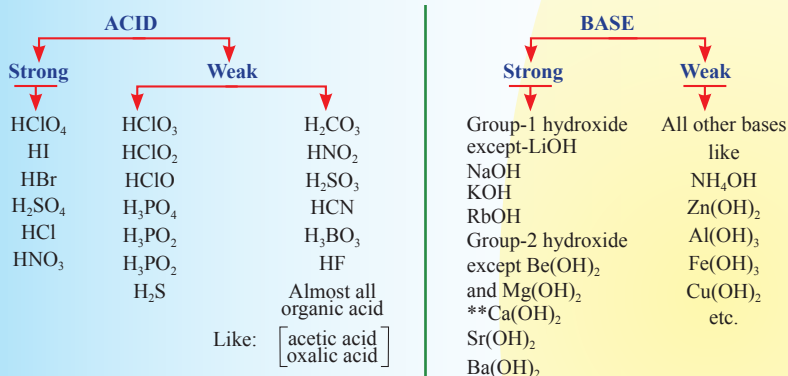
$$0 = \Delta G^\circ + RT \ln K_c \quad \text{or} \quad \Delta G^\circ = -RT \ln K_c \quad \text{or} \quad \ln K_c = (-\Delta G^\circ/RT)$$

Case I: If $\Delta G^\circ < 0$, then $(-\Delta G^\circ/RT)$ is positive, i.e., $e^{(-\Delta G^\circ/RT)} > 1$ hence $K_c > 1$, which implies a spontaneous reaction, i.e., the reaction proceeds in the forward reaction.

Case II: If $\Delta G^\circ > 0$, then $(-\Delta G^\circ/RT)$ is negative, i.e., $e^{(-\Delta G^\circ/RT)} < 1$, hence $K_c < 1$, which implies a non-spontaneous reaction or the reaction proceeds in the forward direction to a very small extent i.e., only a very small quantity of product is formed.



Ionic Equilibrium



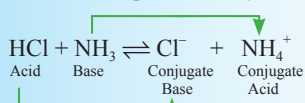
ACID BASE THEORIES (Arrhenius Concept)

| Acid | Base |
|---|---|
| Which produce H ⁺ ion in aqueous solution. e.g. HCl, H ₂ SO ₄ , HClO ₄ , H ₃ PO ₄ , CH ₃ COOH but H ₃ BO ₃ is not a Arrhenius acid. Major Limitation: Defined only in water solvent. | Which produce OH ⁻ ion in aqueous solution. e.g. NaOH, Mg(OH) ₂ , Ba(OH) ₂ |

Bronsted – Lowry Concept

Acid: Which gives H⁺ in any solvent.

Base: Which accepts H⁺ in any solvent



Major Limitation: Does not explain acidic behaviour of aprotic acids e.g. SO₂, CO₂, AlCl₃, SiCl₄

- To find conjugate base of any Acid → Remove one H⁺
- To find conjugate acid of any Base → add one H⁺
- Water is Amphiprotic solvent (can accept as well as lose H⁺)



| LEWIS THEORY | |
|---|--|
| ACID | BASE |
| TYPES OF LEWIS ACID | TYPES OF LEWIS BASE |
| Lewis acid is an electron pair acceptor. | |
| 1. Having Incomplete octet: BF ₃ , BCl ₃ , B(OH) ₃ , AlCl ₃ etc. | 1. Neutral molecule having lone pair $\ddot{\text{N}}\text{H}_3$, R - $\ddot{\text{N}}\text{H}_2$, R ₂ - $\ddot{\text{N}}\text{H}$, H - $\ddot{\text{O}}$ - H, R - $\ddot{\text{O}}$ - R etc. |
| 2. Having vacant d-orbitals: SF ₄ , SF ₆ , SnCl ₂ , SnCl ₄ etc. | |
| 3. Having multiple bonds between atoms of different EN: CO, SO ₂ , SO ₃ etc. | 2. Anions: O ²⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ , Cl ⁻ , Br ⁻ , I ⁻ , CH ₃ COO ⁻ etc. <ul style="list-style-type: none"> All the Lewis bases are Bronsted bases but all the Lewis acids are not Bronsted acids. All Arrhenius acids are Bronsted acid but it is not so for bases. |
| 4. Cations Ag ⁺ , Li ⁺ , Al ⁺³ , Mg ²⁺ False cations (which cannot act as Lewis acid):] NH ₄ ⁺ , H ₃ O ⁺ , PH ₄ ⁺ etc. | |

| OSTWALD'S DILUTION LAW | |
|--|--|
| OSTWALD'S DILUTION LAW (Only for weak electrolytes) $\alpha \propto \sqrt{\text{dilution}}$ dilution $\uparrow \Rightarrow \alpha \uparrow$ | FOR PURE WATER |
| EXPLANATION OF WATER H ₂ O \rightleftharpoons H ⁺ + OH ⁻ K _w = Ionic product of water pK _w = pH + pOH K = dissociation constant of water K = $\frac{K_w}{[\text{H}_2\text{O}]}$ [· [H ₂ O] = 55.5] | 1. [H ⁺] = [OH ⁻] 2. pH = pOH 3. (pH) _{pure water} = $\frac{\text{pK}_w}{2}$ <ul style="list-style-type: none"> pH of an acidic solution is always less than pH of pure water. pH of a basic solution is always greater than pH of pure water. |

HYDROLYSIS OF SALTS

| Salt | Hydrolysis | Resulting solution | Hydrolysis constant (K _h) | Degree of hydrolysis (h) | pH |
|---------------------------|------------|--------------------|---------------------------------------|----------------------------|---|
| Weak acid and Strong base | Anionic | Alkaline pH > 7 | k _w / k _a | $h = \sqrt{\frac{K_h}{C}}$ | $\text{pH} = \frac{1}{2}[\text{pK}_w + \text{pK}_a + \log C]$ |

| Salt | Hydrolysis | Resulting solution | Hydrolysis constant (K_h) | Degree of hydrolysis (h) | pH |
|---------------------------|---------------------------|--|-------------------------------|----------------------------|--|
| Strong acid and Weak base | Cationic | Acidic $\text{pH} < 7$ | k_w / k_b | $h = \sqrt{\frac{K_h}{C}}$ | $\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_b - \log C]$ |
| Weak acid and Weak base | Anionic and Cationic both | Neutral, $\text{pH} = 7$ (If $K_a = K_b$) | $k_w / (k_a \cdot k_b)$ | $h = \sqrt{K_h}$ | $\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a - \text{p}K_b]$ |

Buffer Solutions

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called **buffer solutions**.

Buffers are classified into two categories:

- **Simple buffers:** These are the solutions of salts of weak acid and weak base. For example, $\text{CH}_3\text{COONH}_4$ (ammonium acetate).
- **Mixed buffers:** These are the mixtures of two solutions. These are further of two types:
 - **Acidic buffers:** These are the solutions of mixtures of weak acid and salt of this weak acid with strong base. For example, $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$. They have pH value lesser than 7.
 - **Basic buffers:** These are the solutions of mixtures of weak base and salt of this weak base with strong acid. For example, $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$. They have the pH value more than 7.
- pH of an acidic buffer:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = \text{p}K_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

(Henderson - Hasselbalch equation)

- pH of an basic buffer:

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Acid}]} = \text{p}K_b + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

$$\text{Buffer capacity} = \frac{\text{No. of moles of acid or base added per litre of buffer}}{\text{Change in pH}}$$

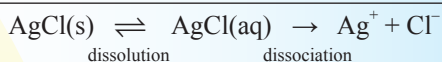
The range of pH over which the buffer solutions remain effective is called **buffer range**.

| Buffer | Buffer range in pH |
|--------|-------------------------------------|
| Acidic | $\text{p}K_a \pm 1$ |
| Basic | $(\text{p}K_w - \text{p}K_b) \pm 1$ |

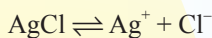
SOLUBILITY (s) & SOLUBILITY PRODUCT (K_{sp})

Solubility

The maximum amount of solute that can be dissolved in a particular amount of solvent at a given temperature is called solubility(s). It is generally expressed in molarity.



Solubility Product (K_{sp})



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

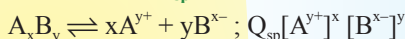
depends only on temperature.

Expressions of K_{sp} : A_xB_y ⇌ xA^{y+} + yB^{x-}

$$\text{General form } K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

$$\text{In terms of 'S': } K_{sp} = (xS)^x (yS)^y$$

Ionic Product [Q_{sp}]



In Q_{sp} the concentration taken are at any time but in K_{sp} the concentration are at equilibrium time/saturation time.

Application

1. If Q_{sp} < K_{sp} [unsaturated]
2. If Q_{sp} = K_{sp} [saturated]
3. If Q_{sp} > K_{sp} [super saturated/ppt. will form]

Effect of Common Ion

Presence of common ion decreases the solubility but has no effect on K_{sp} as it depends only on temperature.

Effect of Odd Ion

Presence of odd ion increases the solubility but has no effect on K_{sp}.

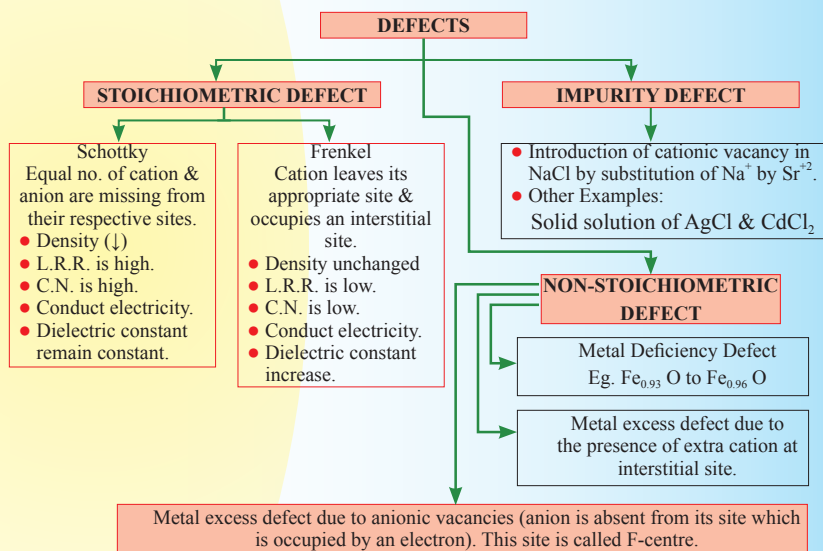
| ACID-BASE TITRATION | | |
|---------------------|-----------------------|-------------------------------------|
| Type of titration | pH range of titration | Suitable indicators |
| SA/SB. | 3-11 | All indicators (MeOH, HPh etc.) |
| SA/WB | 3-7 | Methyl orange (MeOH) and methyl red |
| WA/SB | 7-11 | Phenolphthalein (HPh) |
| WA/WB | 6.5-7.5 | Phenol red |

KEY TIPS

- Buffer capacity $\frac{\text{No. of moles of acid/base added per litre}}{\text{change in pH of buffer solution}}$
- Maximum buffer action when $[\text{salt}] = [\text{acid}]$
- pH of Amphiprotic species: (NaHPO_4 , NaHCO_3) which can donate as well as accept H^+ $\text{pH} = \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2}$



Solid State



Density

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

| | | | |
|----------------|-----|---------------|----|
| CONTRIBUTION | | CORNERS | 8 |
| AT CORNER | 1/8 | FACES | 6 |
| AT FACE | 1/2 | EDGES | 12 |
| AT EDGE | 1/4 | BODY CENTRE | 1 |
| AT BODY CENTRE | 1 | BODY DIAGONAL | 4 |
| | | FACE DIAGONAL | 12 |
| | | FACE CENTRES | 6 |
| | | EDGE CENTRES | 12 |

| Limiting Radius Ratio | Coordination No. of Cation | Geometry of Void | Void found in | Location of void | No. of void per atom | Example |
|--------------------------|----------------------------|------------------|---------------|---|----------------------|---|
| $0.155 \leq r/R < 0.225$ | 3 | Plane Trigonal | — | — | — | Boron oxide (B ₂ O ₃) |
| $0.225 \leq r/R < 0.414$ | 4 | Tetrahedral | FCC, HCP | On body diagonal at $\sqrt{3}a/4$ distance from corner of the unit cell | 2 | ZnS, SiO ₂ , Na ₂ O, CaF ₂ |
| $0.414 \leq r/R < 0.732$ | 6 | Octahedral | FCC, HCP | Body centre & edge centre | 1 | NaCl, MgO |
| $0.732 \leq r/R < 1.000$ | 8 | Cubical | SCC | Body centre | 1 | CsCl |





Classification of solid on the basis of nature of order of arrangement of constituent particles.

| CRYSTALLINE | AMORPHOUS |
|---|--|
| These solids have definite characteristic shape | These solids have irregular shape. |
| Definite melting point & heat of fusion | Indefinite melting point & heat of fusion. |
| Cleavage surfaces are smooth | Cleavage surface are irregular. |
| Anisotropic in nature. | Isotropic in nature. |
| Long range order. | Short range order. |
| Ex.: NaCl, Quartz, Metal, Diamond etc. | Ex. Glass, Quartz Glass, Rubber, Plastics etc. |

| Name of system | Axis | Axis | Bravais Lattices |
|-----------------------------|-------------------|---|--------------------|
| 1. Cubic | $a = b = c$ | $\alpha = \beta = \gamma = 90^\circ$ | SCC, BCC, FCC |
| 2. Tetragonal | $a = b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$ | SCC, BCC |
| 3. Orthorhombic or Rhombic | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$ | SCC, BCC, FCC, ECC |
| 4. Monoclinic | $a \neq b \neq c$ | $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$ | SCC, ECC |
| 5. Triclinic | $a \neq b \neq c$ | $\alpha = \beta \neq \gamma \neq 90^\circ$ | SCC |
| 6. Rhombohedral or Trigonal | $a = b = c$ | $\alpha = \beta = \gamma \neq 90^\circ$ | SCC |
| 7. Hexagonal | $a = b \neq c$ | $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ | SCC |

| S. No. | Type of Ionic Crystal | Geometry | Coordination Number | No. of formula per U.C. | Examples |
|--------|-----------------------------|--|---------------------|--|--|
| 1. | NaCl (1:1) (Rock salt Type) | <ul style="list-style-type: none"> → Cl⁻: Every element of CCP → Na⁺: At Every OHV | 6 : 6 | $4\text{Na}^+ + 4\text{Cl}^-$ 4NaCl (4) | <ul style="list-style-type: none"> ● Halides of (Li, Na, K, Rb); Oxides & sulphides of ● Alkaline earth metals; (some exception) ● AgF, AgCl, AgBr, NH₄X |
| 2. | CsCl Type (1 : 1) | <ul style="list-style-type: none"> → Cl⁻: At Every Corner → Cs⁺: At Body centre | 8 : 8 | $1\text{Cs}^+ + 1\text{Cl}^-$ 1CsCl (1) | <ul style="list-style-type: none"> ● Halides of 'Cs' ● TlCl, TlBr, CaS |

| S. No. | Type of Ionic Crystal | Geometry | Coordination Number | No. of formula per U.C. | Examples |
|--------|---|--|---|--|---|
| 3. | ZnS Type (1:1) (Zinc Blende Type) (Sphalerite) | \rightarrow S ²⁻ : Every element of CCP \rightarrow Zn ²⁺ : At 50% of THV or At Alternate THV | 4 : 4 | 4Zn ²⁺ + 4S ²⁻ 4ZnS (4) | BeS, BeO, CaO, AgI CuCl, CuBr, CuI |
| 4. | CaF ₂ Type (1:2) (Fluorite Type) | \rightarrow Ca ²⁺ : Every element of CCP \rightarrow F ⁻ : At every THV | $\begin{matrix} 4\text{Ca}^{2+} & 8\text{F}^{-} \\ \diagdown & / \\ 8 & : & 4 \end{matrix}$ | 4Ca ²⁺ + 8F ⁻ 4CaF ₂ (4) | BaCl ₂ , BaF ₂ , SrCl ₂ , SrF ₂ , CaCl ₂ , CaF ₂ |
| 5. | Na ₂ O Type (2:1) (Antifluorite Type) | \rightarrow Na ⁺ : At every THV \rightarrow O ²⁻ : Every element of CCP | $\begin{matrix} 8\text{Na}^{+} & 4\text{O}^{2-} \\ \diagdown & / \\ 4 & : & 8 \end{matrix}$ | 8Na ⁺ + 4O ²⁻ 4Na ₂ O (4) | Li ₂ O, Li ₂ S, Na ₂ O Na ₂ S, K ₂ O, K ₂ S |
| 6. | ZnS type (1:1) (Wurtzite) another geometry of ZnS | \rightarrow S ²⁻ : Every Element of HCP \rightarrow Zn ²⁺ : 50% of THV or at alternate THV | 4 : 4 | 6Zn ²⁺ + 6S ²⁻ 6ZnS (6) | Same as Sphalerite |

| S. No. | Contents | SCC | BCC | FCC/CCP | HCP |
|--------|--------------------|---|---|---|---|
| 1. | Geometry |  |  |  |  |
| 2. | Arrangement | AAAA.... Packing but not close packing | ABAB..... Packing but not close packing | ABCABC.... Close Packing or CCP packing | ABAB.... Close Packing |
| 3. | No. of atoms/UC | 1 | 2 | 4 | 6 |
| 4. | Coordination No. | 6 | 8 | 12 | 12 |
| 5. | a & r relation | r = a/2 | r = $\sqrt{3}a/4$ | r = $\sqrt{2}a/4$ | — |
| 6. | Packing Efficiency | $\pi/6$ or 52.4% | $\sqrt{3}\pi/8$ or 68% | $\pi/3\sqrt{2}$ or 74% | $\pi/3\sqrt{2}$ or 74% |
| 7. | Example | Mn | IA ; Group: V & Cr; Ba, Fe | Ca, Sr, Al, Group : Co, Ni, Cu All inert gases except He | Remaining d-block elements, Be & Mg |

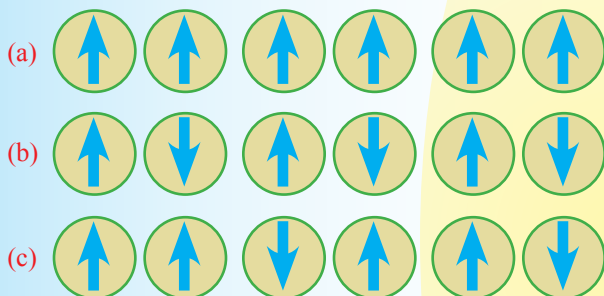
MAGNETIC PROPERTIES

The magnetic properties of different materials are studied in terms of their magnetic moments which arise due to orbital motion and spinning motion of the electrons.

Classification of substances on the basis of magnetic properties:

- Paramagnetic substances are weakly attracted by a magnetic field. They have one or more unpaired electrons and lose their magnetism in the absence of magnetic field, e.g., O₂, Cu²⁺, Fe³⁺, Cr³⁺.
- Diamagnetic substances are weakly repelled by a magnetic field. They have no unpaired electrons and hence have zero magnetic moment, e.g., H₂O, NaCl and C₆H₆.

- Ferromagnetic substances are those which show permanent magnetism even in the absence of magnetic field, as when placed in magnetic field, their unpaired electrons (or magnetic domains) get permanently oriented in one direction, e.g., Fe, Ni, Co, Gd, CrO_2 , etc.
- Antiferromagnetic substances are those which are expected to possess paramagnetism or ferromagnetism but actually have zero net magnetic moment due to equal number of domains in opposite directions, e.g., MnO.
- Ferrimagnetic substances are those expected to have large magnetism but actually have small net magnetic moment due to unequal number of domains in opposite, e.g., magnetite (Fe_3O_4), ferrites like MgFe_2O_4 and ZnFe_2O_4 . These substances lose ferrimagnetism on heating and become paramagnetic.



Schematic alignment of magnetic moments in
(a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic



Solutions

Vapour Pressure: Pressure of any volatile substance at any given temperature.

$$T \uparrow \Rightarrow \text{V.P.} \uparrow$$

$$\text{Attractive Forces} \uparrow \Rightarrow \text{V.P.} \downarrow$$

Raoult's law: Non volatile solute and volatile solvent solution.

$$\text{If } \begin{cases} \text{B} = \text{Non volatile solid} \\ P_B = 0 \end{cases}$$

$$P_A = P_A^\circ X_A$$

Colligative Properties: Properties depends on no. of particles of Non volatile solute in solution.

$$\begin{array}{ccc} \text{No. of particle of} & \uparrow & \text{Colligative} \\ \text{Non volatile solute} & \Rightarrow & \text{Properties} \end{array} \uparrow$$

(1) Relative lowering of V.P. :

$$\frac{P_A^\circ - P_A}{P_A^\circ} = i \frac{n_B}{n_A + n_B} \approx i \frac{n_B}{n_A}$$

where n_B = mole of Non-volatile solute.

i = Vant Hoff's factor.

(2) Elevation in B.P. :

$$\Delta T_b = (T_b^i - T_b) = i \cdot K_b \times m.$$

$$\text{where } K_b = \frac{RT_b^2}{1000 \times l_v}$$

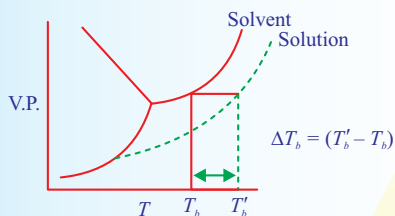
where T_b = B.P. of pure solvent.

l = Latent heat of vapourization per gm

K_b = molal elevation constant

M = Molar mass

$$\text{where } l_v = \left(\frac{\Delta H_{\text{vap}}}{M} \right)$$



(3) Depression in FP.

$$T_f = T_f - T'_f = i k_f \times m$$

$$\text{where } k_f = \frac{RT_f^2}{1000 \times \ell_f}$$

T_f = f.p. of pure solvent

k_f = molal depression constant

ℓ_f = latent heat of fusion per gm.

(4) Osmotic pressure:

$$\pi \propto (P_A^\circ - P_A)$$

$$\pi = iC. \text{ S.T.}$$

where π = osmotic pressure

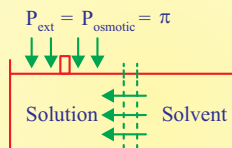
C = molarity (mole/lit)

$S = R = \text{const. for solution.}$

Sol. (1) Sol (2)

If $\pi_1 = \pi_2$ Isotonic

If $\pi_1 > \pi_2$ $\left\{ \begin{array}{l} \text{sol}^n (1) \text{ hypertonic} \\ \text{sol}^n (2) \text{ hypotonic} \end{array} \right.$



Van't Hoff factor for different Cases of solutes undergoing Ionisation and Association

| Solute | Example | Ionisation/association (x degree) | y^* | Van't Hoff factor | Abnormal mol. wt. (m_1') |
|---------------------|----------------------------|---|-------|-------------------|------------------------------|
| Non-electrolyte | urea-glucose, sucrose etc. | none | 1 | 1 | normal mol.wt. |
| Ternary electrolyte | $K_2SO_4, BaCl_2$ | $A_2B \rightleftharpoons 2A^+ + B^{2-}$ $1-x$ $2x$ x | 3 | $(1 + 2x)$ | $\frac{m_1}{(1 + 2x)}$ |

| Solute | Example | Ionisation/association (x degree) | y* | Van't Hoff factor | Abnormal mol. wt. (m ₁ ') |
|-----------------------------------|---|--|---------------|---|--|
| Electrolyte | K ₃ [Fe(CN) ₆], | $A_2B \rightleftharpoons A^{3+} + 3B^{3-}$ <small>$\frac{1-x}{x}$</small> | 4 | (1 + 3x) | $\frac{m_1}{(1+3x)}$ |
| A ₂ B, AB ₃ | FeCl ₃ | | | | |
| Associated Solute | benzoic acid in benzene | $2A \rightleftharpoons A_2$ | $\frac{1}{2}$ | $\left(\frac{1-x}{2}\right) = \left(\frac{2-x}{2}\right)$ | $\frac{2m_1}{(2-x)}$ |
| | forming dimer | $A \rightleftharpoons \frac{1}{2}A_2$ <small>$\frac{(1-x)}{x/2}$</small> | | | |
| | any solute | $nA \rightleftharpoons A_n$ | $\frac{1}{n}$ | $\left[1 + \left(\frac{1}{n}-1\right)x\right]$ | $\left[\frac{m_1}{1 + \left(\frac{1}{n}-1\right)x}\right]$ |
| | forming polymer A _n | $A \rightleftharpoons \frac{1}{n}A_n$ <small>$\frac{(1-x)}{n \cdot x/2}$</small> | | | |
| General | one mole of solute giving y mol of products | $A \rightleftharpoons yB$ | y | $\frac{[1 + (y-1)x]}{x}$ | $\frac{m_1}{[1 + (y-1)x]}$ |

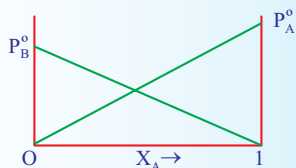
* number of products form one mole solute

Raoult's Law

(1) Volatile binary liquid mix:

| | | |
|-------------------|-------------|------------------------------------|
| Volatile liq. | A | B |
| Mole fraction | X_A / Y_A | $X_B / Y_A \Rightarrow$ liq/vapour |
| V.P. of pure liq. | P_A° | P_B° |

Binary liquid solution:

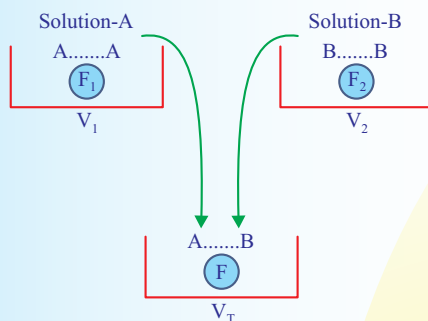


$$\text{By Raoult's law} \Rightarrow P_T = P_A^\circ X_A + P_B^\circ X_B = P_A + P_B \quad \dots(i)$$

$$\text{By Dalton's law} \Rightarrow P_A = Y_A P_T \quad \dots(ii)$$

$$P_B = Y_B P_T \quad \dots(iii)$$

Ideal and Non-Ideal Solution



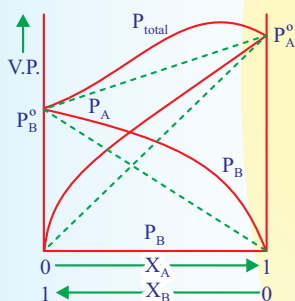
$$\text{Ideal solution : } \begin{cases} F_1 = F_2 = F \\ V_T = V_1 + V_2 \end{cases} \Rightarrow \Delta H_{\text{solution}} = 0$$

Non-Ideal Solution

(1) Solution showing +ve deviation :

$$F < F_1 \text{ \& } F_2$$

$$V_T > V_1 + V_2 \quad \Delta H_{\text{solution}} > 0$$

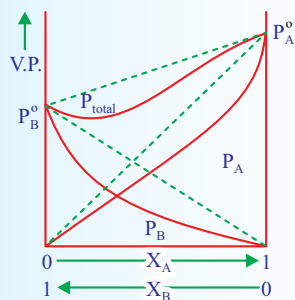


(2) Solution showing -ve deviation:

$$\Rightarrow F > F_1 \text{ \& } F_2$$

$$\Rightarrow V_T < (V_1 + V_2)$$

$$\Rightarrow \Delta H_{\text{solution}} < 0$$



Deviation from Raoult's Law

| | Positive deviation ($\Delta H = +ve$) | Negative deviation ($\Delta H = -ve$) | Zero deviation ($\Delta H = 0$) |
|-------|---|--|--------------------------------------|
| (i) | ethanol + cyclohexane | acetone + chloroform | benzene + toluene |
| (ii) | acetone + carbon disulphide n-hexane + n-heptane | benzene + chloroform | |
| (iii) | acetone + benzene | nitric acid + chloroform | ethyl bromide + ethyl iodide |
| (iv) | ethanol + acetone | acetone + aniline | chlorobenzene + bromobenzene |
| (v) | ethanol + water | water + nitric acid | |
| (vi) | carbon tetrachloride + chloroform | diethyl ether + chloroform | |

Azeotropic mixtures: Some liquids on mixing form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. An azeotropic mixture cannot be separated by fractional distillation.

Types of Azeotropic mixtures

- (i) **Minimum boiling Azeotropic mixtures:** The mixture of two liquids whose boiling point is less than either of the two pure components. They are formed by non-ideal solutions showing positive deviation. For example 95.5% ethanol + 4.5% water boils at 351.15 K.
- (ii) **Maximum boiling Azeotropic mixtures:** The mixture of two liquids whose boiling point is more than either of the two pure components. They are formed by non-ideal solutions showing negative deviation. For example HNO_3 (68%) + water (32%) mixture boils at 393.5 K.



Electrochemistry

ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).

An electrode and its electrolyte comprise an **Electrode Compartment**.

Electrochemical cells can be classified as:

- (i) **Electrolytic Cells** in which a non-spontaneous reaction is driven by an external source of current.
- (ii) **Galvanic Cells** which produce electricity as a result of a spontaneous cell reaction.



NOTES

In a **galvanic cell**, cathode is positive with respect to anode.

In a **electrolytic cell**, anode is made positive with respect to cathode.

REPRESENTATION OF A CELL (IUPAC CONVENTIONS)

Let us illustrate the convention taking the example of Daniel cell.

- (i) Anodic half cell is written on left and cathodic half cell on right hand side.



- (ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.
- (iii) EMF (electromotive force) may be written on the right hand side of the cell.
- (iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.



(v) Inert electrodes are represented in the bracket



RELATIONSHIP BETWEEN ΔG AND ELECTRODE POTENTIAL

Let n , Faraday charge is taken out from a cell of e.m.f. (E) then electrical work done by the cell may be calculated as,

$$\text{Work done} = \text{Charge} \times \text{Potential} = nFE$$

From thermodynamics we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system if there is no work due to volume expansion.

$$\therefore \Delta G = -nFE$$

$$\text{Under standard state} \quad \Delta G^0 = -nFE^0 \quad (i)$$

- (i) From thermodynamics we know, $\Delta G =$ negative for spontaneous process. Thus from eq. (i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.
- (ii) When $\Delta G =$ positive, $E =$ negative and the cell process will be non spontaneous.

| Reactions | ΔG | E |
|-----------------|------------|-----|
| Spontaneous | (-) | (+) |
| Non-spontaneous | (+) | (-) |
| Equilibrium | 0 | 0 |

Standard free energy change of a cell may be calculated by electrode potential data.

Substituting the value of E^0 (i.e., standard reduction potential of cathode-standard reduction potential of anode) in eq. (i) we may get ΔG^0 .

CONCEPT OF ELECTROMOTIVE FORCE (EMF) OF A CELL

Electron flows from anode to cathode in external circuit due to a pushing effect called or electromotive force (e.m.f.). EMF is called as cell potential. Unit of e.m.f. of cell is volt.

EMF of cell may be calculated as:

$$E_{\text{cell}} = \text{reduction potential of cathode} - \text{Reduction potential of anode}$$

Similarly, standard e.m.f. of the cell (E^0) may be calculated as

$$E^0_{\text{cell}} = \text{Standard reduction potential of cathode} - \text{Standard}$$

NERNST EQUATION

Walter Nernst derived a relation between cell potential and concentration of Reaction quotient.

$$\Delta G = \Delta G^0 + RT \ln Q \quad \dots(A)$$

where ΔG and ΔG° are free energy and standard free energy change; 'Q' is reaction quotient.

$$\therefore -\Delta G = nFE \quad \text{and} \quad -\Delta G^\circ = nFE^\circ$$

Thus from E (i), we get $-nFE = -nFE^\circ + RT \ln Q$

$$\text{At } 25^\circ\text{C, above equation may be written as } E = E^\circ - \frac{0.0591}{n} \log Q$$

Where 'n' represents number of moles of electrons involved in process.

E, E° are e.m.f. and standard e.m.f. of the cell respectively.

In general, for a redox cell reaction involving the transference of n electrons

$aA + bB \rightarrow cC + dD$, the EMF can be calculated as:

$$E_{\text{Cell}} = E^\circ_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

(ii) Determination of equilibrium constant: We know, that

$$E = E^\circ - \frac{0.0591}{n} \log Q \quad \dots(i)$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. $E = 0$

\therefore From Eq. (i), we have

$$0 = E^\circ - \frac{0.0591}{n} \log K_{\text{eq}} \quad \text{or} \quad K_{\text{eq}} = \text{anti log} \left[\frac{nE^\circ}{0.0591} \right]$$

(iii) Heat of Reaction inside the cell: Let n Faraday charge flows out of a cell of e.m.f. E, then

$$-\Delta G = nFE \quad (i)$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad (ii)$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T \left[\frac{\partial (-nFE)}{\partial T} \right]_p = \Delta H - nFT \left[\frac{\partial E}{\partial T} \right]_p$$

$$\therefore \Delta H = -nFE + nFT \left[\frac{\partial E}{\partial T} \right]_p$$

(iv) Entropy change inside the cell: We know that $G = H - TS$ or $\Delta G = \Delta H - T\Delta S$...(i)

where ΔG = Free energy change; ΔH = Enthalpy change and ΔS = entropy change. According to Gibbs Helmholtz equation,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \dots \text{(ii)}$$

From Eqs. (i) and (ii), we have

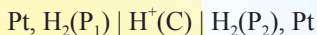
$$-T\Delta S = T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \text{or} \quad \Delta S = - \left[\frac{\partial \Delta G}{\partial T} \right]_p$$

$$\text{or } \Delta S = nF \left[\frac{\partial E}{\partial T} \right]_p$$

CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

(i) Electrode Gas concentration cell:



Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

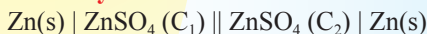
Cell process: $1/2\text{H}_2(p_1) \rightarrow \text{H}^+(\text{c}) + \text{e}^-$ (Anode process)

$$\frac{\text{H}^+(\text{c}) + \text{e}^- \rightarrow 1/2\text{H}_2(p_2)}{1/2\text{H}_2(p_1) \rightleftharpoons 1/2\text{H}_2(p_2)} \quad \therefore E = - \frac{2.303RT}{F} \log \left[\frac{p_2}{p_1} \right]^{1/2}$$

$$\text{or } E = \left[\frac{2.303RT}{2F} \right] \log \left[\frac{p_2}{p_1} \right], \quad \text{At } 25^\circ\text{C}, E = \frac{0.059}{2F} \log \left[\frac{p_1}{p_2} \right]$$

For spontaneity of such cell reaction, $p_1 > p_2$

(ii) Electrolyte concentration cells:



In such cells, concentration gradient arise in electrolyte solutions.

Cell process may be given as,



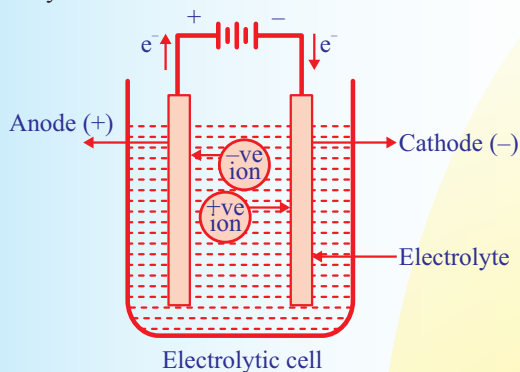
\therefore From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F} \log \left[\frac{\text{C}_1}{\text{C}_2} \right] \quad \text{or} \quad E = \frac{2.303RT}{2F} \log \left[\frac{\text{C}_2}{\text{C}_1} \right]$$

For spontaneity of such cell reaction, $\text{C}_2 > \text{C}_1$

ELECTROLYSIS

The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.



ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy.

The entire assembly except that of the external battery is known as the electrolytic cell.

ELECTRODES

The metal strip at which positive current enters is called **anode**; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called cathode. Cathodes are negatively charged.

| | | | |
|---------|----------|---|-------------------------|
| Anode | Positive | Loss of electron or oxidation takes place | Positive current enters |
| Cathode | Negative | Gain of electron or reduction takes place | Current leaves |

FARADAY'S LAWS OF ELECTROLYSIS:

- (i) **First law of electrolysis:** Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$$w \propto Q$$

W = weight liberated, Q = charge in coulomb

$$w = ZQ$$

Z = electrochemical equivalent

when Q = 1 coulomb, then w = Z

Thus, weight deposited by 1 coulomb charge is called electrochemical equivalent.

let 1 ampere current is passed till 't' seconds.

Then, $Q = It$ $\therefore w = ZIt$

1 Faraday = 96500 coulomb = Charge of one mole electrons.

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.

$$Z = \frac{\text{Eq. wt. of the substance}}{96500}$$

- (ii) **Second law of electrolysis:** When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. i.e. $w_1/w_2 = E_1/E_2$

CONDUCTANCE

Introduction: Both metallic and electrolytic conductors obey Ohm's law.

i.e.

$$V = IR$$

where V = Potential difference in volt; I = Current in ampere; R = resistance in Ohm.

We know, resistance is directly proportional to length of conductor and inversely proportional to cross sectional area of the conductor.

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho \frac{l}{A} \quad (\rho = \text{Specific resistance})$$

Specific resistance is the resistance of a conductor having length of 1 cm and cross sectional area of 1 cm².

Unit of R is ohm and unit of specific resistance is ohm cm.

Reciprocal of resistance is called as conductance and reciprocal of specific resistance is called as specific conductance.

$$\frac{1}{R} = \frac{1A}{\rho l} \quad \text{or} \quad C = K \frac{A}{l}$$

where C = conductance ohm⁻¹; K = specific conductance ohm⁻¹ cm⁻¹.

Mho and siemens are other units of conductance

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

Specific conductance = Cell constant – Conductance

Specific conductance is conductance of 1 cm³ of an electrolyte solution.

In case of electrolytic solution, the specific conductance is defined as the conductance of a solution of definite concentration enclosed in a cell having two electrodes of unit area separated by 1 cm apart.

- 1. Equivalent Conductance:** Equivalent conductance is the conductance of an electrolyte solution containing 1 gm equivalent of electrolyte. It is denoted by Λ .

$$\Lambda = K \times V$$

$$(\Lambda = \text{ohm}^{-1} \text{ cm}^{-1} \times \text{cm}^3 = \text{ohm}^{-1} \text{ cm}^2)$$

Usually concentration of electrolyte solution is expressed as C gm equivalent per liter.

$$\text{Thus, } V = \frac{1000}{C}$$

{Volume having 1 gm equivalent electrolyte in the solution}

$$\text{Thus, } \Lambda = K \times \frac{1000}{C}$$

- 2. Molar Conductance:** Molar conductance may be defined as conductance of an electrolyte solution having 1 gm mole electrolyte in a liter. It is denoted by Λ_m .

$$\Lambda_m = K V$$

Usually concentration of electrolyte solution is expressed as 'M' gm mole electrolyte per liter.

$$\text{Thus, } V = \frac{1000}{M}$$

$$\text{Hence, } \Lambda_m = K \times \frac{1000}{M}$$

Relation between Λ and Λ_m :

Application of Kohlrausch's Law

- (A) Determination of Λ_m^0 of a weak electrolyte:

In order to calculate Λ_m^0 of a weak electrolyte say CH_3COOH , we determine experimentally Λ_m^0 values of the following three strong electrolytes:

- A strong electrolyte containing same cation as in the test electrolyte, say HCl.
- A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa .
- A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

Λ_m^0 of CH_3COOH is then given as:

$$\Lambda_m^0 \text{ of } (\text{CH}_3\text{COOH}) = \Lambda_m^0 (\text{HCl}) + \Lambda_m^0 (\text{CH}_3\text{COONa}) - \Lambda_m^0 (\text{NaCl})$$

Proof:

$$\Lambda_m^0(\text{HCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-} \quad \dots(\text{i})$$

$$\Lambda_m^0(\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^0 + \lambda_{\text{Na}^+} \quad \dots(\text{ii})$$

$$\Lambda_m^0(\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-} \quad \dots(\text{iii})$$

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$$\Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{CH}_3\text{COO}^-}^0 = \Lambda_m^0(\text{CH}_3\text{COOH})$$

(B) Determination of degree of dissociation (α):

$$\alpha = \frac{\text{Number of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^0}$$

(C) Determination of solubility of sparingly soluble salt:

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to Λ_m^0 as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (D).

$$\Lambda_m^0 = \frac{1000K}{C}$$

where C is the molarity of solution and hence the solubility.



Chemical Kinetics

- **Rate of reaction (ROR)** = $\frac{\text{Rate of disappearance of reactant (appearance of products)}}{\text{Stoichiometric coefficient of reactant (products)}}$

- **For a reaction:**

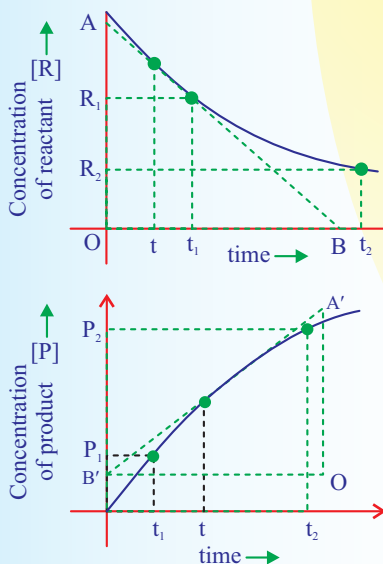


- **Instantaneous rate:** $-\frac{1}{a} \left(\frac{d[A]}{dt} \right) = -\frac{1}{b} \left(\frac{d[B]}{dt} \right) = \frac{1}{c} \left(\frac{d[C]}{dt} \right) = \frac{1}{d} \left(\frac{d[D]}{dt} \right)$

Relationship between rate of reaction and rate of disappearance of reactant (rate of appearance of product).

- **Average rate:** $-\frac{1}{a} \left(\frac{\Delta[A]}{\Delta t} \right) = -\frac{1}{b} \left(\frac{\Delta[B]}{\Delta t} \right) = \frac{1}{c} \left(\frac{\Delta[C]}{\Delta t} \right) = \frac{1}{d} \left(\frac{\Delta[D]}{\Delta t} \right)$

⇒ Graphical method for determining rate:



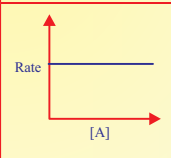
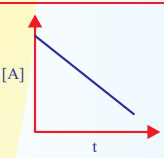
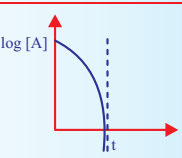
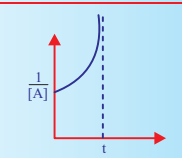
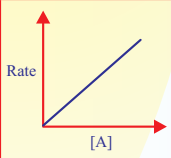
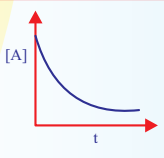
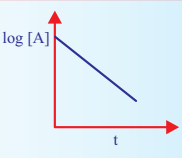
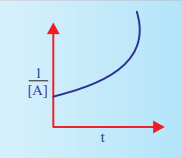
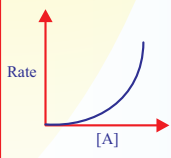
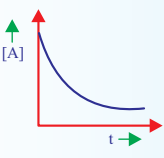
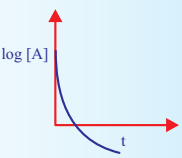
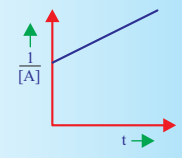
$$\text{Avg. Rate} = -\left(\frac{[R]_2 - [R]_1}{t_2 - t_1}\right) = \frac{([P]_2 - [P]_1)}{t_2 - t_1}$$

$$\text{Instantaneous rate} = -\left(\frac{OA}{OB}\right) = +\frac{OA'}{OB'} = \pm \text{slope of tangent}$$

Important kinetic expression for reaction of type A → B:

| Order | Zero | 1st | 2nd | nth |
|-------------------------------|---|---------------------------------------|--|--|
| Differential rate law | Rate = k | Rate = k[A] | Rate = k[A] ² | Rate = k[A] ⁿ |
| Integrated rate law | [A] ₀ - [A] = kt | kt = ln $\frac{[A]_0}{[A]}$ | kt = $\frac{1}{[A]} - \frac{1}{[A]_0}$ | kt = $\frac{1}{(n-1)} \left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$ |
| Half life (t _{1/2}) | t _{1/2} = $\frac{[A]_0}{2k}$ | t _{1/2} = $\frac{\ln 2}{k}$ | t _{1/2} = $\frac{1}{[A]_0 k}$ | t _{1/2} = $\frac{1}{k(n-1)} \left[\frac{2^{n-1} - 1}{[A]_0^{n-1}} \right]$ |
| t _{3/4} | t _{3/4} = 1.5 t _{1/2} | t _{3/4} = 2 t _{1/2} | t _{3/4} = 3 t _{1/2} | t _{3/4} = (2 ⁿ⁻¹ + 1)t _{1/2} |

Graphs of Various Order

| Order | Rate vs [A] | [A] vs t | log [A] vs t | $\frac{1}{[A]}$ vs t |
|--------------|---|---|---|---|
| Zero order |  |  |  |  |
| First order |  |  |  |  |
| Second order |  |  |  |  |

Where

[A]₀ ⇒ initial concentration

[A] ⇒ concentration at time t

$t_{1/2}$ \Rightarrow time taken for initial concentration of reactant to finish by 50%

$t_{3/4}$ \Rightarrow time taken for initial concentration of reactant to finish by 75%

Monitoring Kinetics Experimentally

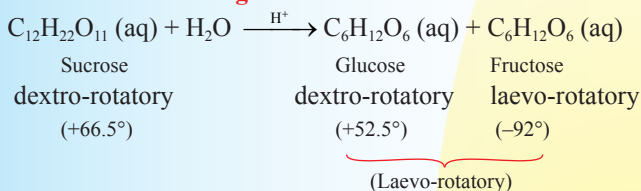
The kinetics of reaction can be followed (i.e. order, rate constant etc., can be established) by measuring a property which changes with time.

e.g. (i) Total pressure in a gaseous reaction.

$$k = \frac{1}{t} \ln \left(\frac{P_0}{P_0 - x} \right)$$

Example: (For Monitoring Kinetics Experimentally)

(i) Inversion of cane sugar:



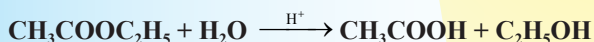
$$k = \frac{2.303}{t} \log \left(\frac{r_\infty - r_0}{r_\infty - r_t} \right)$$

r_0 = rotation at time, $t = 0$

r_t = rotation at time, $t = t$

r_∞ = rotation at time, $t = \infty$

(ii) Acidic hydrolysis of ethyl acetate:



$$k = \frac{2.303}{t} \log \left(\frac{V_\infty - V_0}{V_\infty - V_t} \right)$$

V_0 = Volume of NaOH solution used at time, $t = 0$

V_t = Volume of NaOH solution used at time, $t = t$

V_∞ = Volume of NaOH solution used at time, $t = \infty$



NOTES

Here NaOH acts as a reagent. Acetic acid is one of the product the amount of which can be found by titration against standard NaOH solution. But being an acid-catalysed reaction, the acid present originally as catalyst, also reacts with NaOH solution.

Important characteristics of first order reaction

- $t_{1/2}$ is independent of initial concentration.
- In equal time interval, reactions finishes by equal fraction.

| | | | | |
|----------------|---------|---------|----------|----------------|
| | $t = 0$ | $t = t$ | $t = 2t$ | $t = 3t \dots$ |
| Reactant conc. | a_0 | a_0x | a_0x^2 | $a_0x^3 \dots$ |

$x =$ fraction by which reaction complete in time 't'.

- Graph of $\ln [A]$ vs t is straight line with slope = $-\frac{k}{2.303}$
- Graph of $[A]$ vs t is exponentially decreasing.

Zero order

- $t_{1/2}$ of zero order is directly proportional to initial concentration.
- In equal time interval, reaction finishes by equal amount.

| | | | |
|---------|-----------|------------|------------------|
| $t = 0$ | $t = t$ | $t = 2t$ | $t = 3t \dots$ |
| C_0 | $C_0 - x$ | $C_0 - 2x$ | $C_0 - 3x \dots$ |

- Graph of $[A]$ vs t is straight line.

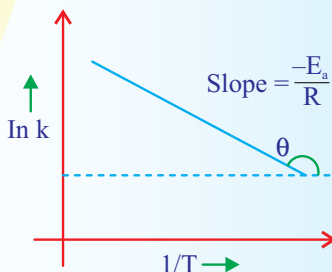
A zero order reaction finishes in $t = \frac{[A]_0}{k}$

Temperature dependence

- Arrhenius equation : $k = A \cdot e^{-E_a/RT}$
- E_a = minimum energy over and above the average energy of reactant which must be possessed by reacting molecule for collision to be successful.
- A = frequency factor - proportional to number of collisions per unit volume per second.
- $e^{-E_a/RT}$ = Fraction of collision in which energy is greater than E_a .
- A and E_a are constant i.e. do not vary with temperature

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

Graph: Graphical determination of E_a .

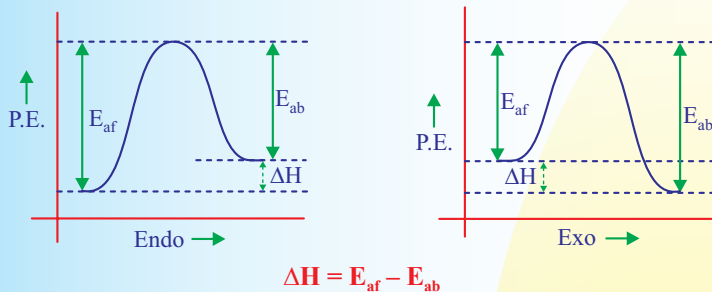


$$\text{Temperature coefficient} = \frac{k_{T+10}}{k_T}$$

By default $T = 298\text{K}$

$$\text{Variation of rate constant with temperature} \Rightarrow \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Endothermic and exothermic reactions:



$$\Delta H = E_{af} - E_{ab}$$



- (i) Rate = $(k_1 + k_2) [A]$ - (differential rate law)
- (ii) $\frac{k_1}{k_2} = \frac{[B]}{[C]}$
- (iii) $t_{1/2} = \frac{0.693}{k_1 + k_2}$
- (iv) % of B = $\frac{k_1}{k_1 + k_2} \times 100$; % of C = $\frac{k_2}{k_1 + k_2} \times 100$
- (v) $[A] = [A]_0 e^{-(k_1 + k_2)t}$

Pseudo-order reaction:

Rate law \rightarrow rate = $k [A]^m [B]^n$

Pseudo rate law:

rate = $k_1 [A]^m$

[B] assumed constant in two cases:

- (i) B in large excess
- (ii) B \rightarrow CATALYST



Surface Chemistry

CLASSIFICATION BASED ON INTERACTION OF PHASES

LYOPHILIC AND LYOPHOBIC SOLS

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion medium, are called lyophilic sols (solvent - liking).

For example: Dispersion of gelatin, starch, gum and proteins in water.

Colloidal solutions in which the dispersed phase has no affinity or attraction for the medium or for the solvent are called Lyophobic colloidal (Solvent hating) solutions.

COMPARISON OF LYOPHOBIC AND LYOPHILIC SOLS

| Property | Lyophilic sol (Emulsoid) | Lyophobic sol (suspensoid) |
|---------------------------|--|---|
| 1. Preparation | Can be easily prepared by shaking or warming the substance with solvent | Can not be prepared easily special methods are required |
| 2. Stability | are more stable | are less stable |
| 3. Reversibility | are reversible | are irreversible |
| 4. Viscosity | Viscosity is much higher than that of solvent | Viscosity is nearly same as that of the solvent |
| 5. Surface tension | Surface tension is usually low | Surface tension is almost same as that of solvent |
| 6. Hydration or solvation | These are highly solvated as the particles have great affinity for solvent | These are less solvated as the particles have less affinity for the solvent |
| 7. Charge | The particles have little charge or no charge at all | The particles carry a characteristic charge either positive or negative |
| 8. Visibility | Particles can not be seen under microscope | Particles can be seen under microscope |

| Property | | Lyophilic sol (Emulsoid) | Lyophobic sol (suspensoid) |
|----------|------------------------------|---|--|
| 9. | Coagulation or precipitation | Precipitated by high concentration of electrolytes | Precipitated by low concentration of electrolytes |
| 10. | Tyndall effect | Less Scattering | More Scattering |
| 11. | Migration in electric field | May or may not migrate as they may or may not carry charge. | Migrate towards anode or cathode as these particles carry charge. |
| 12. | General Ex. | Mostly or organic nature Ex. Gelatin, Starch, Gum, Albumin & Cellulose Solution | Mostly of Inorganic nature Ex. Transition metal salt in water like Gold, As etc. |

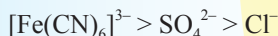
PEPTIZATION

The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed as peptization. The electrolyte used is called a **Peptizing agent**.

Hardy Schulze Rule: This rule states that the precipitating effect of an ion on dispersed phase of opposite charge increases with the valency of the ion.

The higher the valency of the flocculating ion, the greater is its precipitating power. Thus for the precipitation of As_2S_3 sol (-ve) the precipitating power of Al^{3+} , Ba^{2+} , and Na^+ ions is in the order $Al^{3+} > Ba^{2+} > Na^+$.

Similarly for preparing $Fe(OH)_3$ sol (positive) the precipitating power of $[Fe(CN)_6]^{3-}$, SO_4^{2-} and Cl^- ions is in the order.



The minimum concentration of an electrolyte in milli moles required to cause precipitation of 1 litre sol in 2 hours is called FLOCCULATION VALUE. The smaller the flocculating value, the higher will be the coagulating power of the ion.

$$\text{Flocculation value} \propto \frac{1}{\text{Flocculation power}}$$

GOLD NUMBER

The number of milligrams of a hydrophilic colloid that will just prevent the precipitation of 10 ml of standard gold sol on addition of 1 ml of 10% NaCl solution is known as **Gold number** of that protector (Lyophilic colloid).

The precipitation of the gold sol is indicated by a colour change from red to blue when the particle size just increases.

The **smaller the gold number** of a protective Lyophilic colloid, **greater is its protection power**.



Gelatin and starch have the maximum & minimum protective power.

$$\text{Protection Capacity} \propto \frac{1}{\text{Protection Number (Gold number)}}$$

TYPES OF COLLOIDS ACCORDING TO THEIR SIZE

| Multi Molecular | Macro Molecular | Associated colloids |
|--|---|--|
| Formation by aggregation of a large number of atoms or smaller molecules of substance. | Formation by aggregation of big size molecules. These are polymer with high molecular mass. | These are the substances which behave as normal electrolytes at low concentration but get associated at higher concentration and behave as colloidal solutions. These associated particles are also called micelles. |
| Ex. → Gold Sol (Au) Sulphur sol (S ₈) | Ex. → Starch, Cellulose, Protein etc. | Ex. → Soap & Detergent |

COMPARISON OF PHYSI-SORPTION AND CHEMI-SORPTION

| | Physical Adsorption | Chemical Adsorption (Activated ad.) |
|----|--|--|
| 1. | It is caused by intermolecular vander waal's forces. | It is caused by chemical bond formation. |
| 2. | It is not specific. | It is highly specific. |
| 3. | It is reversible. | It is irreversible. |
| 4. | Heat of adsorption is low. (20–40) KJ/mol | Heat of adsorption is high. (80–240 KJ/mol) |
| 5. | No appreciable activation is energy is involved. | High activation energy involved. |
| 6. | If forms multimolecular layers on adsorbent surface. | If forms unimolecular layer under high pressure. |

Critical temperature increases
Ease of liquification increases
Extent of adsorption increases (true for physisorption)

GENERAL CHARACTERISTICS OF CATALYSTS

- (i) A catalyst remains unchanged in mass and chemical composition but can change their physical state.

- (ii) Only a very small amount of catalyst is sufficient to catalyse a reaction.
- (iii) A catalyst does not initiate a reaction.
- (iv) Solid catalyst is more efficient when used in finely divided form.
- (v) generally catalyst does not change the nature of products.
- (vi) A catalyst does not change the equilibrium state of a reversible reaction but helps to achieve the equilibrium state or position of equilibrium in lesser time.
- (vii) The catalyst are generally specific in nature.
- (viii) Changes rate constant of reaction.
- (ix) Does not change free energy of reaction.
- (x) Participates in mechanism or reaction.

Charge on colloidal particles: Colloidal particles always carry an electric charge. The nature of this charge is same on all the particles in a given colloidal solution and may be either positive or negative. The charge is due to preferential adsorption of ions from solution.

Origin of charge on colloidal sol particles:

- Colloidal sol particles carry charge. Charge on sol particles may arise due to any of the following reasons : by friction, ionisation and adsorption.
- Colloidal sol particles adsorb their own ions from the solution and become charged, e.g., when KI is added to AgNO_3 solution, silver iodide, AgI is formed which adsorbs silver ions, Ag^+ and becomes positively charged.



- However when AgNO_3 is added to potassium iodide solution, silver iodide is precipitated which adsorbs iodide ions from the solution and becomes negatively charged.



| Positively Charged Sols | Negatively Charged Sols |
|--|---|
| Hydrated metallic oxides. e.g., $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, metal hydroxides, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, basic dye stuff like Prussian blue, haemoglobin (blood). | Metals, e.g., Cu, Ag, Au, Metallic sulphides – e.g., As_2S_3 , CdS, acidic dyes like eosin, congo red, etc., sols of gelatin, gum, starch, etc. |



Organic Chemistry

Some Basic Principles and Techniques

Electrophiles are electron deficient species.

e.g. H^{\oplus} , R^{\oplus} , NO_2^{\oplus} , X^{\oplus} , PCl_3 , PCl_5

(NH_4^{\oplus} and H_3O^{\oplus} are not electrophile)

Nucleophiles are electron rich species.

e.g. Cl^{\ominus} , CH_3^{\ominus} , OH^{\ominus} , RO^{\ominus} , CN^{\ominus} , $\ddot{N}H_3$, $R\ddot{O}H$, $CH_2=CH_2$, $CH\equiv CH$

Relative electron withdrawing order (-I order)

$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -COOH > -X > -OR > -OH$
 $> -C\equiv CH > -NH_2 > -C_6H_5 > -CH=CH_2$

Relative electron releasing order (+I order)

$-\overset{\ominus}{N}H > -O^{\ominus} > -COO^{\ominus} > 3^{\circ} \text{ alkyl} > 2^{\circ} \text{ alkyl} > 1^{\circ} \text{ alkyl} > -CH_3$

RELATIVE STABILITY ORDER

(A) Stability of carbocation

$\text{Cyclohexadienyl}^{\oplus} > (Ph)_3\overset{\oplus}{C} > (Ph)_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 > (CH_3)_3\overset{\oplus}{C} >$
 $(CH_3)_2\overset{\oplus}{C}H > CH_3\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H > CH\equiv\overset{\oplus}{C}$

(B) Stability of free radical

$(Ph)_3\dot{C} > (Ph)_2\dot{C}H > Ph\dot{C}H_2 > CH_2=CH-\dot{C}H_2 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H$
 $> CH_3\dot{C}H_2 > \dot{C}H_3$

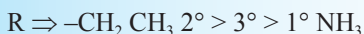
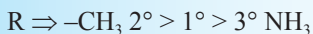
(C) Stability of carbanion

$(Ph)_3\overset{\ominus}{C} > (Ph)_2\overset{\ominus}{C}H > Ph-\overset{\ominus}{C}H_2 > CH_2=CH-\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_3 > CH_3\overset{\ominus}{C}H_2$
 $> (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

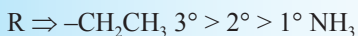
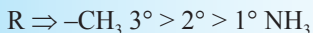
$$\text{BASIC STRENGTH} \propto K_b \propto \frac{1}{pK_b}$$

- **Basic strength of amine:**

- **In aqueous medium**



- **In gaseous medium**



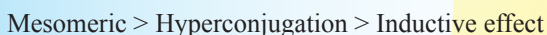
- **Reactivity towards nucleophile (NAR)**



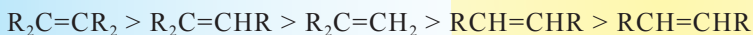
- **Reactivity order towards acyl nucleophilic substitution reaction**



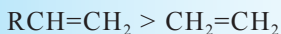
- **Order of electronic effect**



- **Stability of alkene \propto no. of α -hydrogen**



trans form cis form

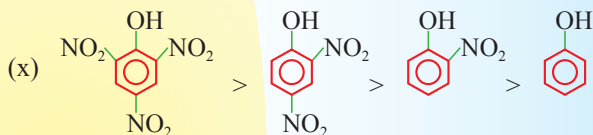
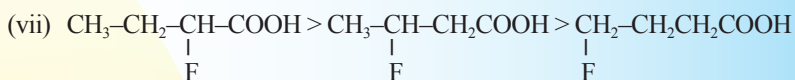
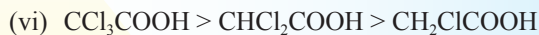
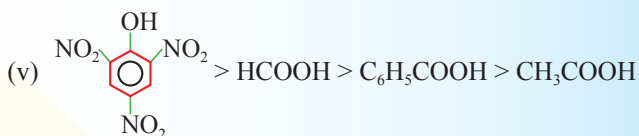


- **Heat of hydrogenation $\propto \frac{1}{\text{Stability of alkene}}$**

ACIDIC STRENGTH \propto STABILITY OF CONJUGATE BASE

$$\propto K_a \propto \frac{1}{pK_a}$$





PURIFICATION METHODS (Distillation Techniques)

Type:

(A) Simple Distillation

Conditions

- When liquid sample has non volatile impurities.
- When boiling point difference is 30 K or more.

Examples

- Mixture of chloroform
(BP = 334K) and Aniline
(BP = 475K)

- (ii) Mixture of Ether
(b.p. = 308K) &
Toluene (b.p. = 384K)
- (iii) Hexane (342K) and
Toulene (384K)

(B) Fractional Distillation

When b.p. difference is 10K

Examples

- (i) Crude oil in petroleum industry
- (ii) Acetone (329 K) and Methyl alcohol (338K)

(C) Distillation under Reduced Pressure (Vacuum Distillation)

When liquid boils at higher temperature and it may decompose before b.p. is attained.

Examples

- (i) Concentration of sugar juice
- (ii) Recovery of glycerol from spent lye.
- (iii) Glycerol

(D) Steam Distillation

When the substance is immiscible with water and steam volatile.

$$\begin{array}{ccccccc}
 P & = & P_1 & + & P_2 \\
 \text{Vapour} & & \text{Vapour} & & \text{Vapour} \\
 \text{pressure} & & \text{pressure} & & \text{pressure} \\
 & & \text{of} & & \text{of water} \\
 & & \text{Organic} & & \\
 & & \text{liquid} & &
 \end{array}$$

Examples

- (i) Aniline is separated from water
- (ii) Turpentine oil
- (iii) Nitro Benzene
- (iv) Bromo Benzene
- (v) Naphthalene
- (vi) O-Nitrophenol

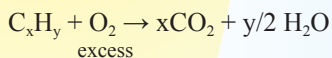
LASSAIGNE'S METHOD

(detection of elements)

| Element | Sodium extract | Confirmed test |
|-------------------------------|---|--|
| Nitrogen | Na+C+N $\Delta\downarrow$ NaCN | (NaCN+FeSO ₄ +NaOH) boil and cool +FeCl ₃ +conc. HCl→Fe ₄ [Fe(CN) ₆] ₃ Prussian blue colour |
| Sulphur | 2Na+S $\Delta\downarrow$ Na ₂ S | (i) Na ₂ S+Na ₂ [Fe(CN) ₅ NO] sodium nitrosorpuside →Na ₄ [Fe(CN) ₅ NOS] a deep violet colour (ii) Na ₂ S+CH ₃ COOH+(CH ₃ COO) ₂ Pb→ A black ppt. (PbS↓) |
| Halogen | Na+X $\Delta\downarrow$ NaX | NaX+HNO ₃ +AgNO ₃ (i) White ppt. soluble in aq. NH ₃ confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH ₃ confirms Br. (iii) Yellow ppt. insoluble in aq. NH ₃ confirms I. |
| Nitrogen and sulphur together | Na+C+N+S $\Delta\downarrow$ NaCNS Sodium thiocyanate (Blood red colour) | As in test for nitrogen; insted of green or blue colour, blood red colouration confirms presence of N and S both |

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Extimtion of carbon and hydrogen-Leebig's method



$$\% \text{ of C} = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of org. compd}} \times 100$$

$$\% \text{ of H} = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{wt. of org. compd}} \times 100$$

NOTES

This method is suitable for estimation if organic compound contains C and H only. In case if other elements e.g., N, S, halogens are also present the organic compound will also give their oxides which is being absorbed in KOH and will increase the percentage of carbon and therefore following modification should be made.

ESTIMATION OF NITROGEN

Duma's method: The nitrogen containing organic compound yields nitrogen gas on heating it with copper (II) oxide in the presence of CO₂ gas. The mixture of gases is collected over potassium hydroxide solution in which CO₂ is absorbed and volume of nitrogen gas is determined.

$$\% \text{ of N} = \frac{28}{22400} \times \left(\frac{\text{Vol. of N}_2 \text{ collected at N.T.P.}}{\text{Wt. of organic compound}} \right) \times 100$$



NOTES

This method can be used to estimate nitrogen in all types of organic compounds.

Kjeldahl's method: In this method nitrogen containing compound is heated with conc. H₂SO₄ in presence of copper sulphate to convert nitrogen into ammonium sulphate which is decomposed with excess of alkali to liberate ammonia. The ammonia evolved is

$$\% \text{ of N} = \frac{1.4 \times \text{volume of acid (ml)} \times \text{normality of acid}}{\text{wt. of organic compound}}$$



NOTES

This method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuff, soil, fertilizers and various agricultural products. This method cannot be used for compound having nitro groups, azo group (–N=N–) and nitrogen in the ring (pyridine, quinole etc.) Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.



Isomerism

DEFINITION

Compounds having same molecular formula but differ in atleast one physical or chemical or biological properties are called isomers and this phenomena is known as isomerism.

Types of Isomerism: (A) Structural isomerism (B) Stereo isomerism

(A) STRUCTURAL ISOMERISM

Structural isomerism is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

Types of Structural Isomerism

Chain isomerism: This type of isomerism is due to difference in the arrangement of carbon atoms constituting the chain.

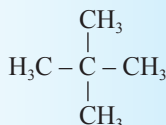
Key points: Parent carbon chain or side chain should be different.

e.g. C_5H_{12} : $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

n-pentane



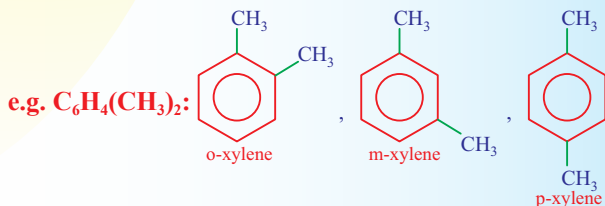
iso-pentane



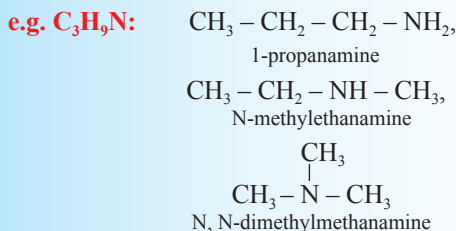
neo-pentane

Positional isomerism: It occurs when functional groups or multiple bonds or substituents are in different positions on the same carbon chain.

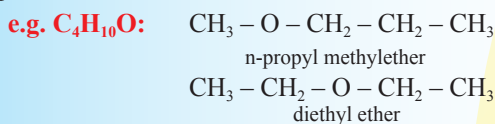
Key points: Parent carbon chain remain same and substituent, multiple bond and functional group changes its position.



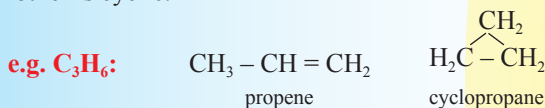
Functional isomerism: It occurs when compounds have the same molecular formula but different functional groups.



Metamerism: This type of isomerism occurs when the isomers differ with respect to the nature of alkyl groups around the same polyvalent functional group.



Ring-Chain isomerism: In this type of isomerism, one isomer is open chain but another is cyclic.

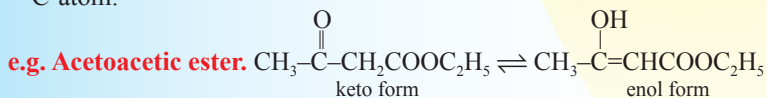


- For chain, positional and metamerism, functional group must be same.
- Metamerism may also show chain and position isomerism but priority is given to metamerism.

Tautomerism: This type of isomerism is due to spontaneous interconversion of two isomeric forms into each other with different functional groups in dynamic equilibrium.

Conditions:

- Presence of $-\overset{\text{O}}{\parallel}{\text{C}}-$ or $-\overset{\text{O}}{\parallel}{\text{N}} \rightarrow \text{O}$
- Presence of at least one α -H atom which is attached to a saturated C-atom.



Enol content enhance by:

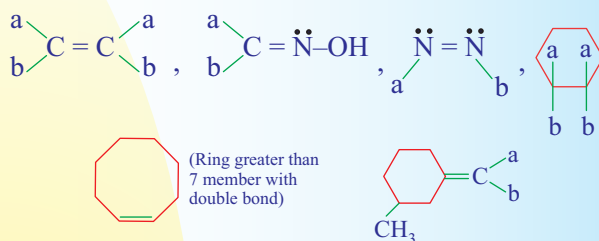
- Acidity of α -H of keto form
- Intra molecular H-Bonding in enol form
- Resonance in enol form
- Aromatisation in enol form

(B) STEREOISOMERISM

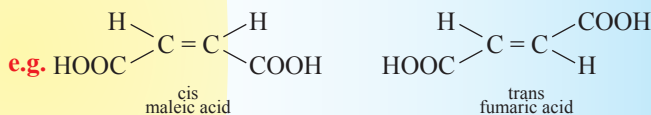
Compounds with the same molecular formula and structural formula but having difference in the spatial arrangement of atoms or groups in 3D space are called stereoisomers and the phenomenon is called stereoisomerism.

Types of Stereoisomerism

Geometrical isomerism: It is due to restricted rotation and is observed in following systems



- **Cis-trans isomerism:** The cis compound is the one with the same groups on the same side of the bond, and the trans has the same groups on the opposite sides. Both isomers have different physical and chemical properties.



- General physical properties of geometrical isomer of but-2-ene

| | |
|---------------------|-------------|
| (i) Stability | trans > cis |
| (ii) Dipole moment | cis > trans |
| (iii) Boiling point | cis > trans |
| (iv) Melting point | trans > cis |

Calculation of number of geometrical isomers:

| | |
|---------------|-----------------------------------|
| Unsymmetrical | 2^n |
| Symmetrical | $2^{n-1} + 2^{m-1}$ |
| | $m = \frac{n}{2}$ (If n is even) |
| | $m = \frac{n+1}{2}$ (If n is odd) |

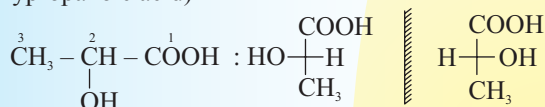
- Where n = number of sites where GI is possible.

Optical isomerism: Compounds having similar molecular and structural formula but differing in the stereo chemical formula and behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomerism.

Types of optical isomers

- (1) Optically active
 - dextrorotatory (*d*)
 - laevorotatory (*l*)
- (2) Optically inactive
 - meso
 - **Condition** Molecule should be asymmetric or chiral i.e. symmetry elements (POS & COS) should be absent.
 - The carbon atom linked to four different groups is called **chiral carbon**.
 - **Fischer projection** An optical isomer can be represented by Fischer projection which is planar representation of three dimensional structure.

Fischer projection representation of lactic acid
(2-hydroxypropanoic acid)



- **Configuration of optical isomer**
 - (a) Absolute configuration (R/S system)
 - (b) Relative configuration (D/L system)
- **Determination of R/S configuration**

Rule-1 Assign the priority to the four groups attached to the chiral carbon according to priority rule.

Rule-2 If lowest priority (4) is bonded to vertical line then moving



Rule-3 If lowest priority (4) is bonded to horizontal line then moving



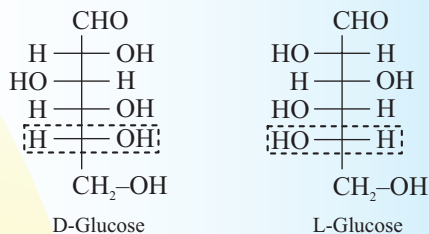
DETERMINATION OF D/L SYSTEM

- Reference molecule glyceraldehyde
- It is used to assign configuration in carbohydrate amino acid and similar compounds.

Rule: Arrange parent carbon chain the vertical line

- Placed most oxidised carbon on the top or nearest to top.

- On highest IUPAC numbered chiral carbon
If OH group on RHS → D
If OH group on LHS → L



CIP SEQUENCE RULE

The following rules are followed for deciding the precedence order of the atoms or groups:-

- (i) Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.
- (ii) In case of isotopes, isotopes having higher atomic mass is given priority.
- (iii) If the first atom of a group attached to asymmetric carbon atom is same then we consider the atomic number of 2nd atom or subsequent atoms in group.
- (iv) If there is a double bond or triple bond, both atoms are considered to be duplicated for triplicated.
 - Non-superimposable mirror images are called **enantiomers** which rotate the plane polarised light up to same extent but in opposite direction.
 - **Diastereomers** are stereoisomers which are not mirror images of each other. They have different physical and chemical properties.
 - **Meso compounds** are those compounds whose molecules are superimposable on their mirror images inspite of the presence of asymmetric carbon atom.
 - An equimolar mixture of the enantiomers (*d* & *l*) is called **racemic mixture**. The process of converting *d*- or *l*- form of an optically active compound into racemic form is called **racemisation**.
 - The process by which *d/l* mixture is separated into *d* and *l* forms with the help of chiral reagents or chiral catalyst is known as **resolution**.
 - Compound containing chiral carbon may or may not be optically active but show optical isomerism.
 - For optical isomer chiral carbon is not the necessary condition.

Calculation of number of optical isomers

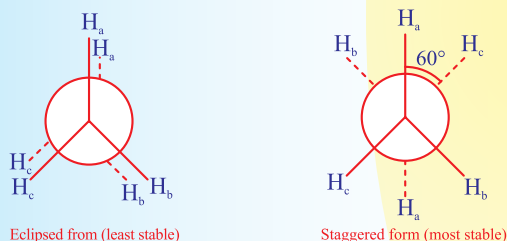
| The compound | Optically active forms | Optically inactive forms (meso) |
|----------------------------|---------------------------|---------------------------------|
| Unsymmetrical | 2^n | Zero |
| Symmetrical If n = even | $2^{(n-1)}$ | $2^{\frac{n}{2}-1}$ |
| Symmetrical If n = odd | $2^{(n-1)} - 2^{(n-1)/2}$ | $2^{(n-1)/2}$ |

* Where n = no. of chiral carbon

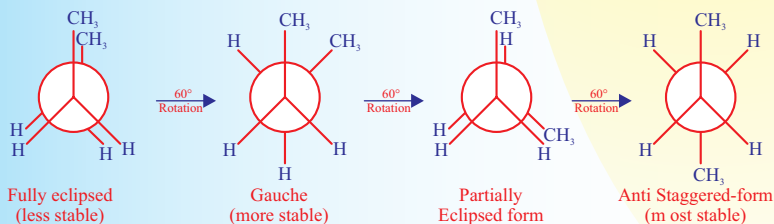
The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by 0-360° are called conformations or conformational isomers or rotational isomers and this phenomenon is called conformational isomers.

CONFORMATIONAL ISOMERISM

Newmann projection: Here two carbon atoms forming the σ bond are represented one by circle and other by centre of the circle. Circle represents rear side C and its centre represents front side carbon. The C–H bonds of front carbon are depicted from the centre of the circle while C–H bond of the back carbon are drawn from the circumference of the circle.



• **Conformations of butane:** $\overset{4}{\text{C}}\text{H}_3 - \overset{3}{\text{C}}\text{H}_2 - \overset{2}{\text{C}}\text{H}_2 - \overset{1}{\text{C}}\text{H}_3$

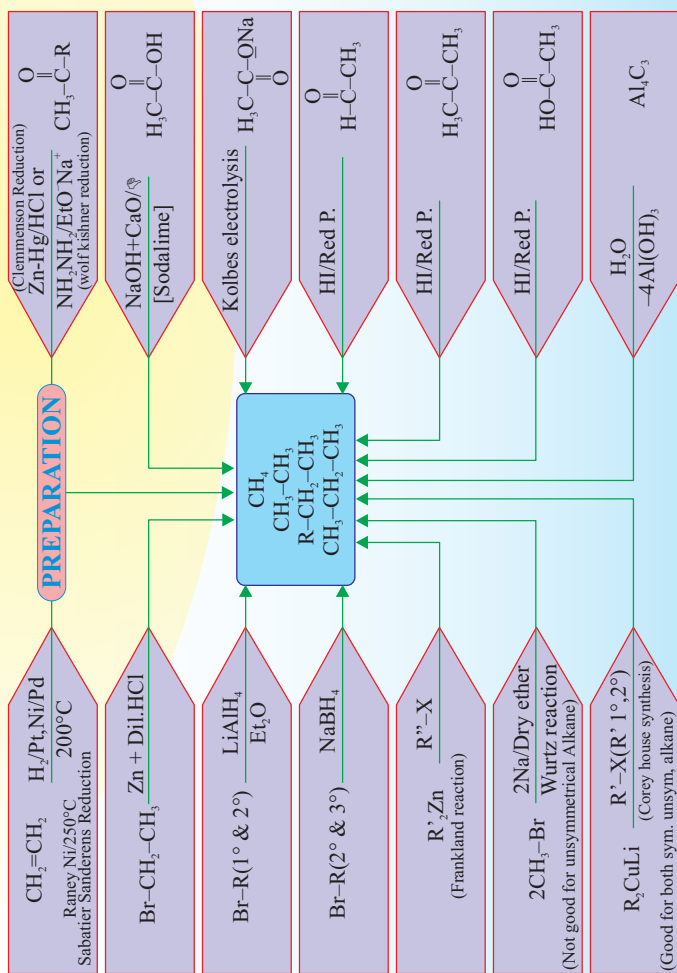


- The order of stability of conformations of n-butane. Anti staggered > Gauche > Partially eclipsed > Fully eclipsed.
- Relative stability of various conformation of cyclohexane is Chair > twist boat > boat > half chair.

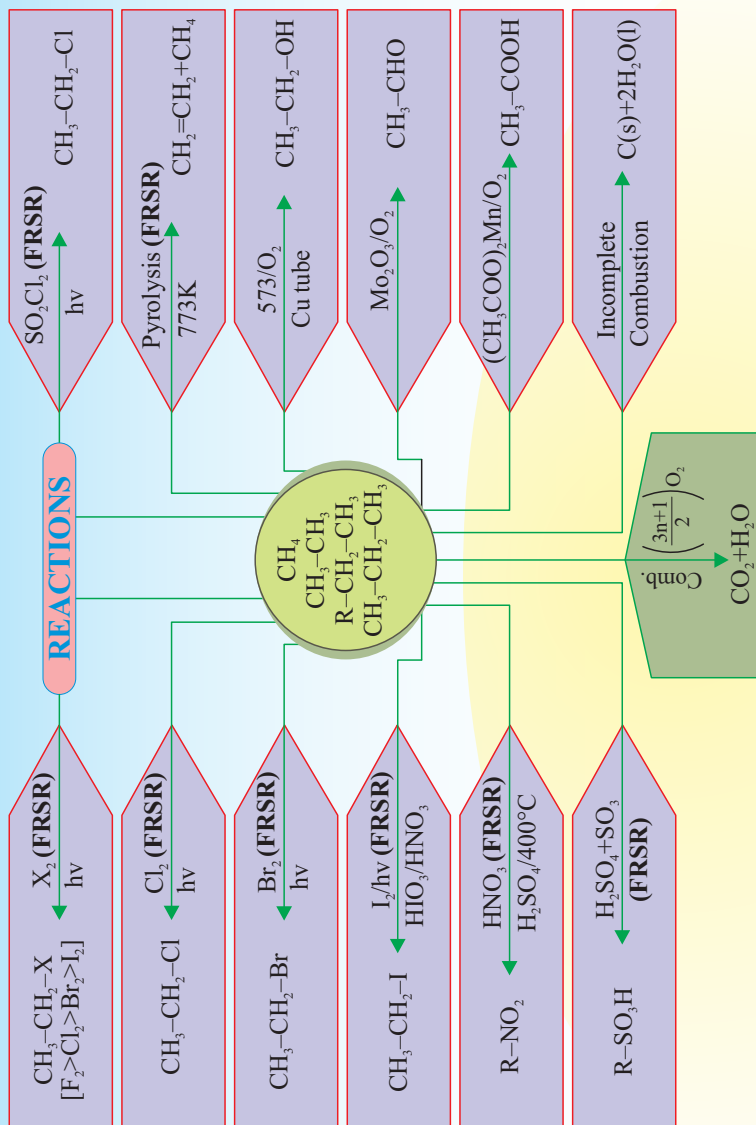


Hydrocarbons

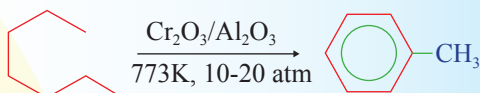
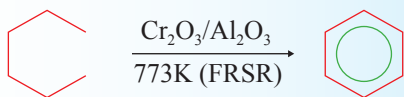
ALKANE



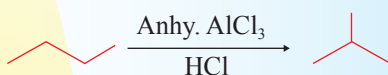
HYDROCARBON OF ALKANE



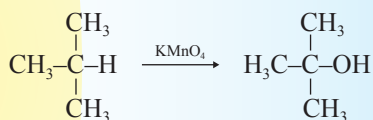
Aromatization



Isomerization



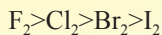
Oxidation at 3°H



- Reactivity of alkane towards free radical halogenation is \propto stability of free radical



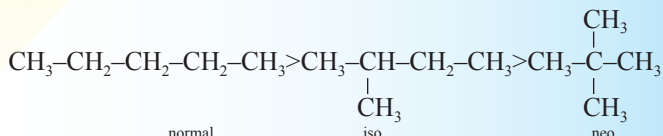
- Reactivity of halogen towards free radical substitution



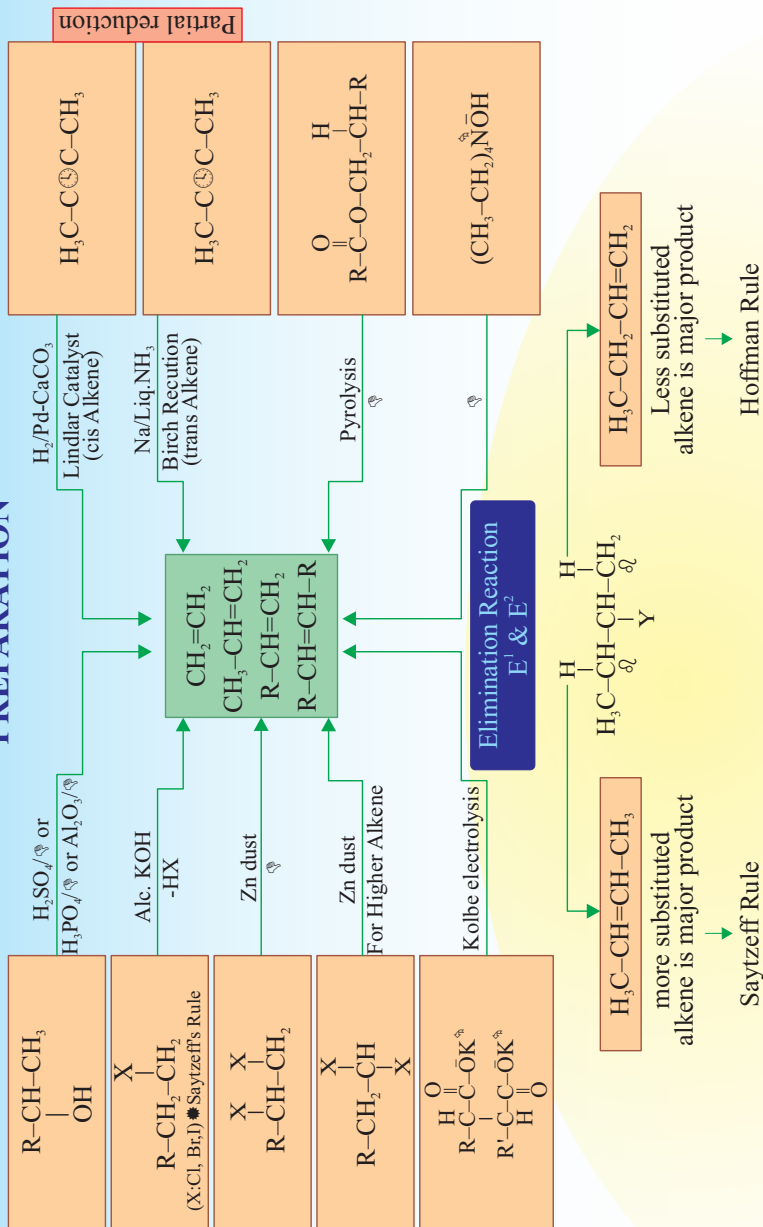
- Knocking tendency of petroleum as fuel decrease with increase in side chain. Straight chain > Branched chain Knocking tendency is in the order



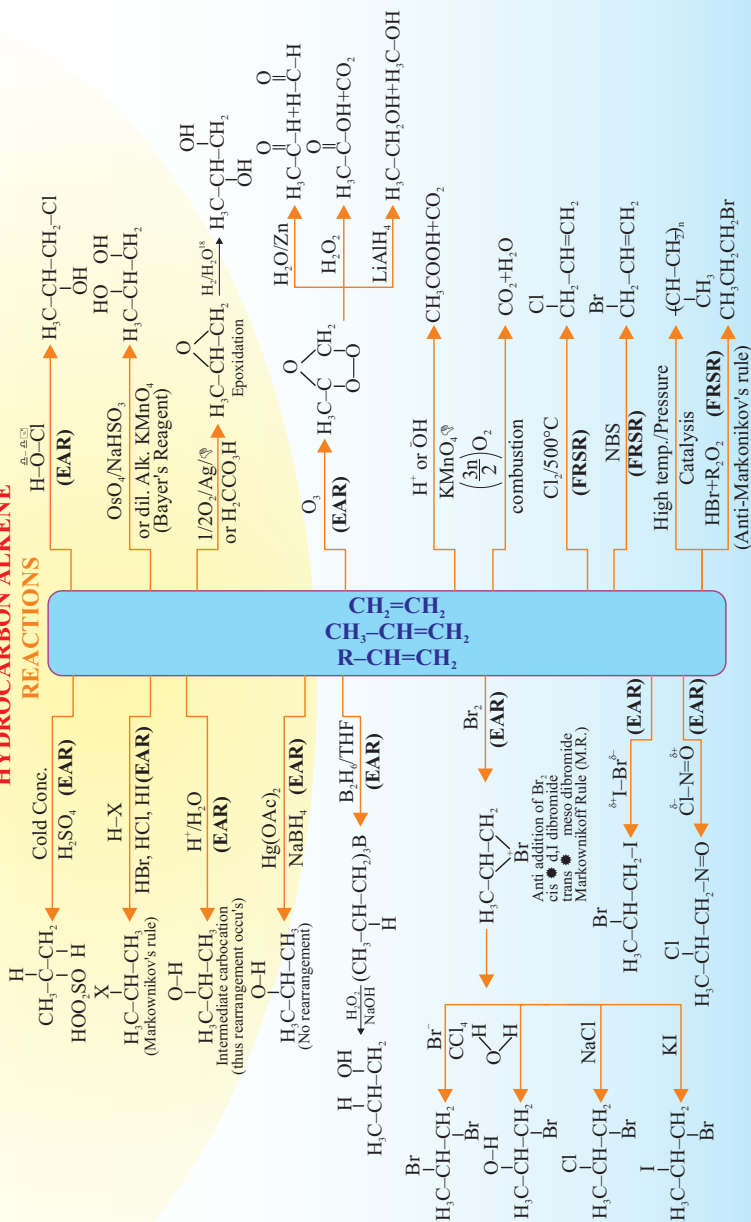
- Boiling point decrease with increase in number of side chain.



HYDROCARBON-ALKENE PREPARATION



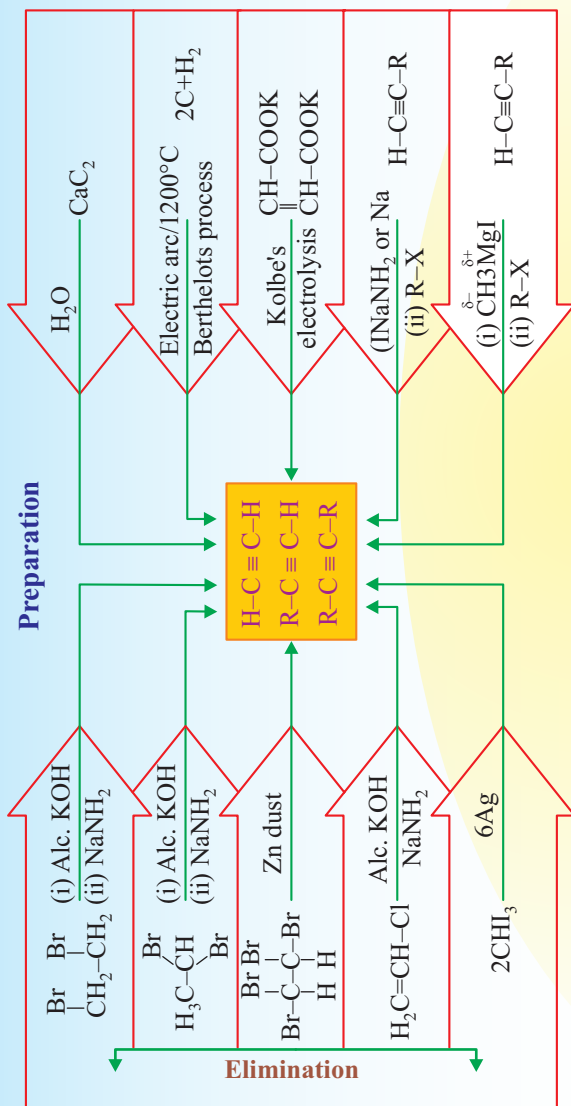
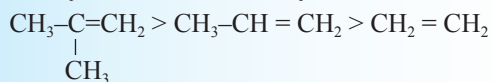
HYDROCARBON ALKENE REACTIONS



(Marknikov's rule) $\text{Br} \leftarrow \text{HBr} \cdot \text{Peroxide}$ $\text{Br} \rightarrow \text{HBr} \cdot \text{Peroxide}$ **(Anti-Marknikov's rule)**

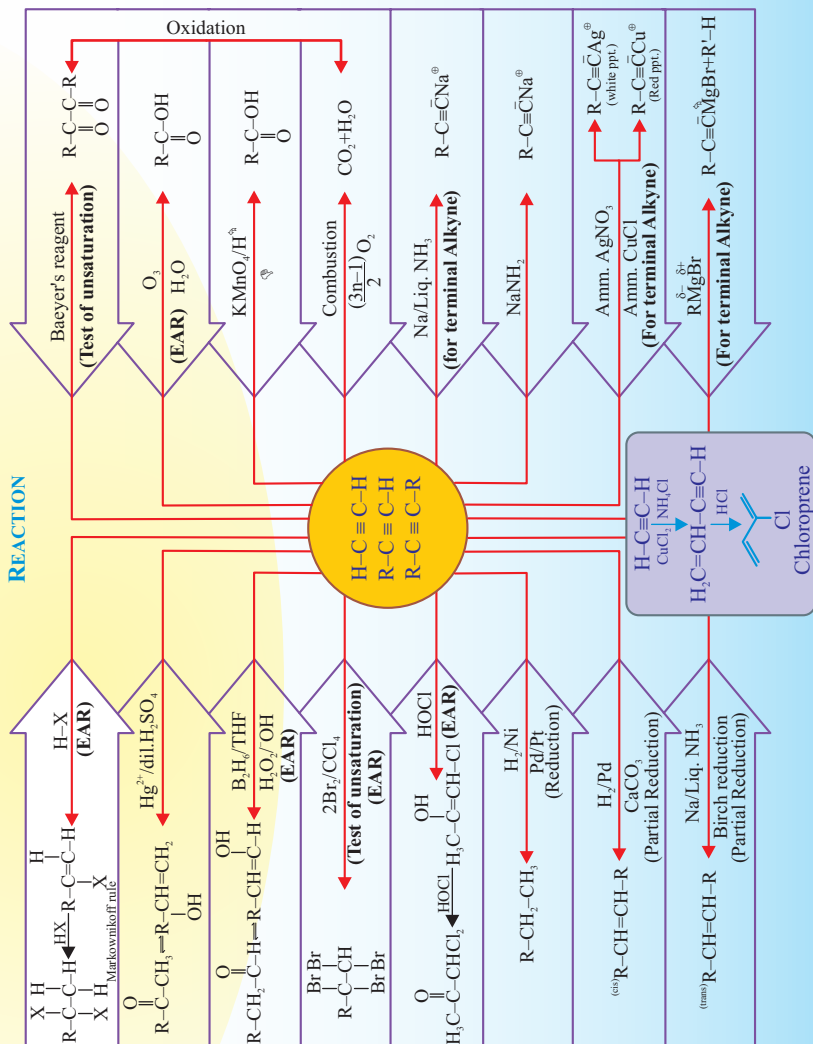
Rate of EAR : R₂C=CR₂ > R₂C=CHR > RCH=CHR > R-CH₂=CH₂ > CH₂=CH₂

- Order of reactivity of olefins for hydrogenation $\text{CH}_2 = \text{CH}_2 > \text{R}-\text{CH}=\text{CH}_2$
(Reverse of stability)
- Order of reactivity of alkene towards hydration

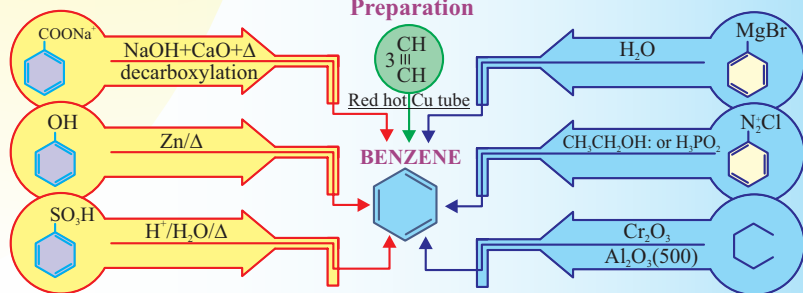


HYDROCARBON-ALKYNE

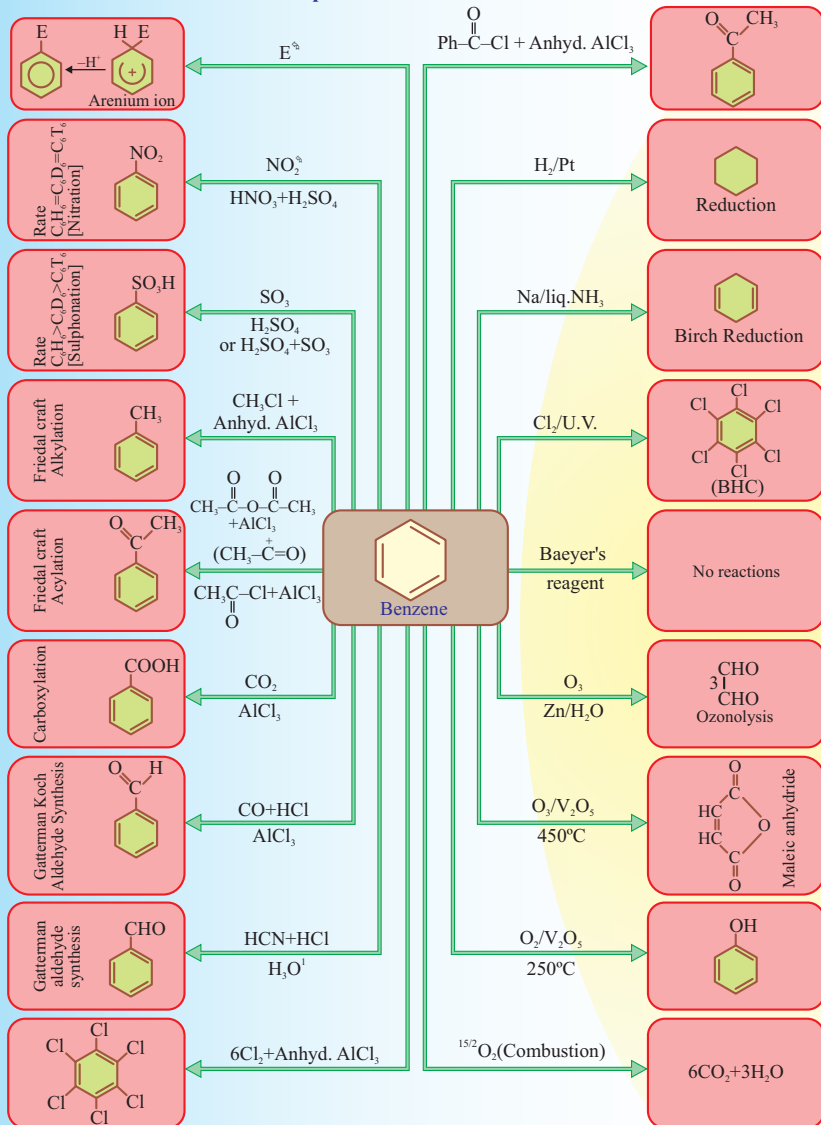
REACTION



Preparation



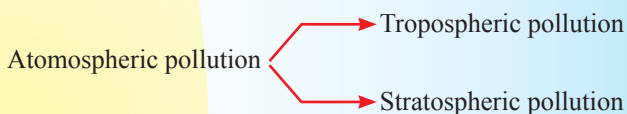
Reaction Electrophilic Substitution Reactions



Environment Pollution

POLLUTANT

Substance which cause pollution is known as pollutant.



Tropospheric pollution occurs due to presence of undesirable solid or gaseous particles in air.

Gaseous Pollutant

SO₂: Cause respiratory diseases of anthma, bronchitis emphysema etc & irrataling to eyes.

NO₂: Form by fossil fuel burn, Damage lungs.

Higer concentration of NO₂ damage the leaves of plant and retard rate of photosynthesis.

Hydrocarbon: Form by incomplete combustion of fuel of automobile, Carcogenic.

Oxide of Carbon

CO: Blocks the delivery of oxygen to organs and tissues.

Carboxy hemoglobine is 300 times more stable then oxy hemoglobin about 3-4% of carboxy hemoglobin the oxygen carrying capacity is highly reduced.

CO₂: Main source is respiration, burning of fossil fuels, demposition of lime stone in cement industry.

Increase of CO₂ cause global warming.

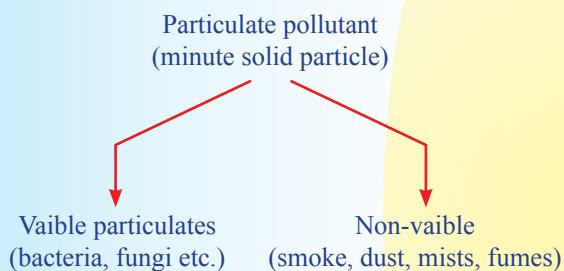
Global Warming and Green House Effect

Some of the gases such as CO_2 , CH_4 , O_3 , CFC(s) and water vapour trapped the heat and does not radiates back to the atmosphere. This cause global warming.

Acid Rain

- Normally the pH rain water is 5.6 due to the reaction between rain water and CO_2 .
- When pH less then 5.6 then it is called acid rain.
- **Source:** burning of fuel (contain N & S) form SO_2 & NO_2 .
- Harmful to agriculture, tree and plants.
- Taj Mahal affect by acid rain.

Particulate Pollutant



Smoke: Solid/mixture of solid and liquid particles formed from burning of fossil fuel, oil smoke etc.

Dust: Find solid particle over $1\mu\text{m}$ diameter, produced by crushin, grinding etc.

Mist: Mist are produced by particle of spray liquid condensation of vapours, eg. herbiciaes mist etc.

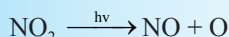
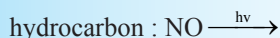


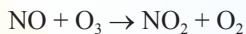
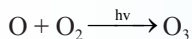
Pb is major air pollutant.

Smog (Smoke + Fog)

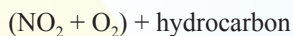
Classical smog: (Smoke + fog + CO_2) also called reducing smog

Photochemical smog:





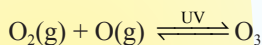
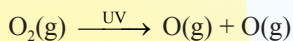
contribute of Haze



CH_2O
 formaldehyde
 or
 $\text{CH}_2 = \text{CHCHO}$
 A.croetin
 or
 $\text{CH}_3\text{COONO}_2$
 peroxy acetyl nitrate (PAN)

Stratospheric Pollution

Formation & decomposition of oxone.

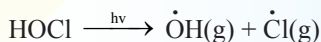
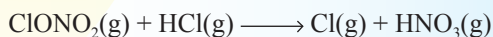
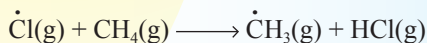
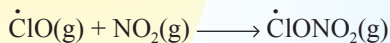
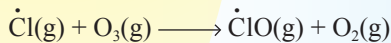
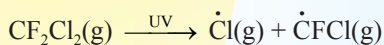


Ozone is thermodynamically unstable and thus dynamic equilibrium exist between production.

Ozone Hole

The main reason of ozone layer depletion the release of CFC(s) (also called as freous).

Reaction of Ozone Depletion



WATER POLLUTION

Cause of Water Pollution

- (i) Pathogen
- (ii) Organic waste
- (iii) Organic waster

BOD: The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called Biochemical **Oxygen Demand (BOD)**. Clean water would have BOD value of less than 5 ppm where as highly polluted water could have a BOD value of 17 ppm or more.

Fluoride: Soluble fluoride is often added to drinking waler to bring its concentration upto 1 ppm or 1 mg dm^{-3} .

However, F^- ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth.

Lead: The prescribed upper limit concentration of lead in drinking water is about 50 ppm. Lead can damage kidney, liver, reproductive system etc.

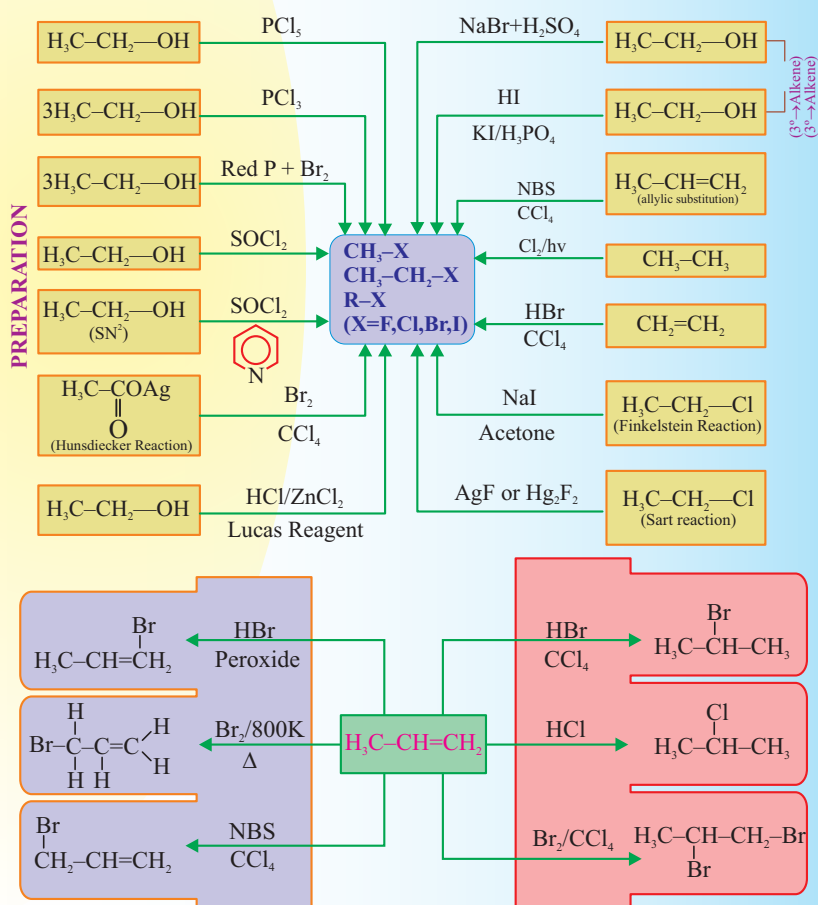
Sulphate: Excessive sulphate (>500 ppm) in drinking water causes laxative effect, otherwise at moderate levels it is harmless.

Nitrate: The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

Table: Maximum Prescribed Concentration of Some Metals in Drinking Water

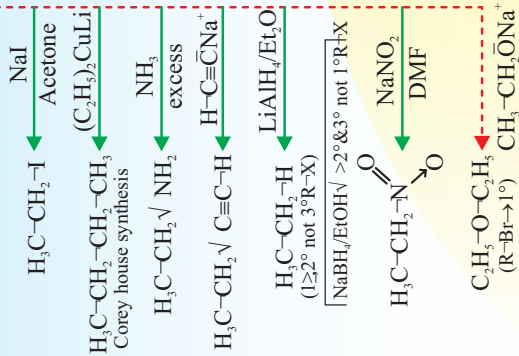
| Metal | Maximum concentration (ppm or mg dm^{-3}) |
|-------|---|
| Fe | 0.2 |
| Mn | 0.05 |
| Al | 0.2 |
| Cu | 3.0 |
| Zn | 5.0 |
| Cd | 0.005 |

Haloalkane and Haloarene

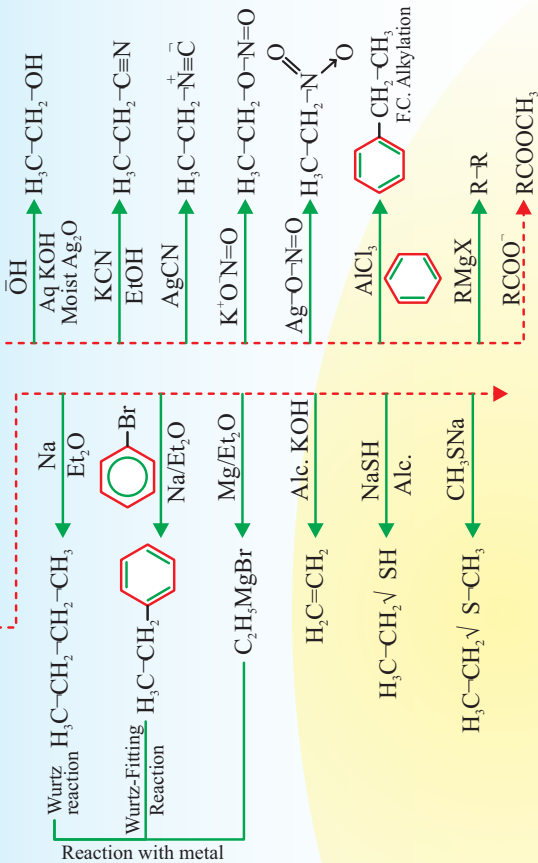


REACTIONS

Nucleophilic substitution
 $S_N1 : 3 > 2 > 1$
 $S_N2 : 1 > 2 > 3$

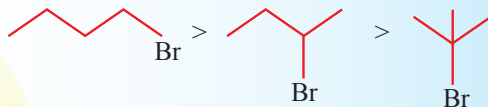


(Reactivity order)
 $(R-I > R-Br > R-Cl > R-F)$
 Ambident Nucleophile: $\bar{C}N, \bar{O}-N=O$

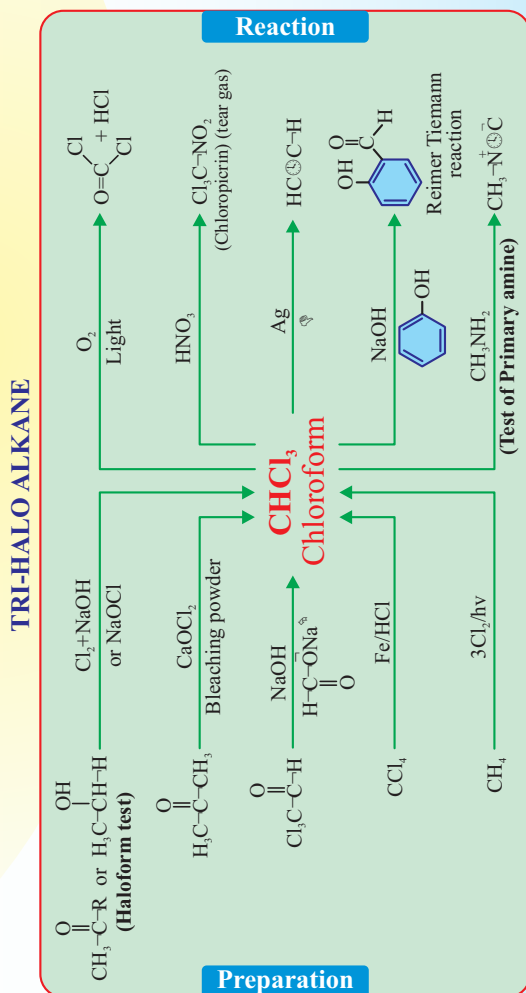


Physical Properties

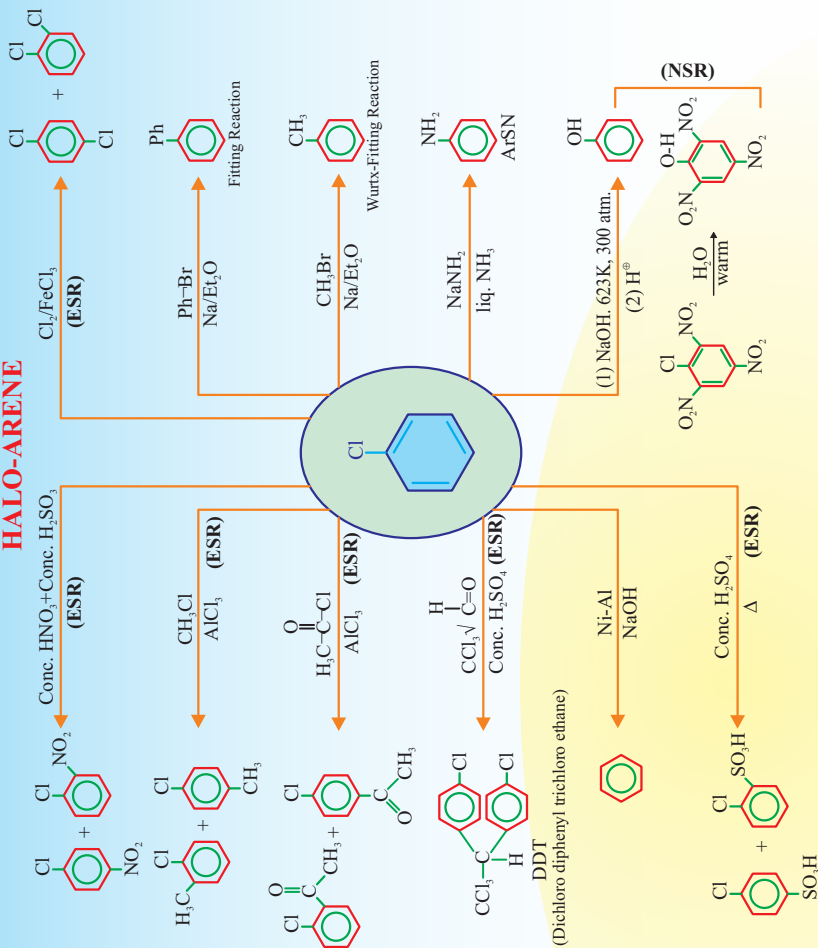
- (1) Dipole moment: $\text{CH}_3\text{-Cl} > \text{CH}_3\text{-F} > \text{CH}_3\text{-Br} > \text{CH}_3\text{-I}$
- (2) Bond enthalpies: $\text{CH}_3\text{-F} > \text{CH}_2\text{-Cl} > \text{CH}_3\text{-Br} > \text{CH}_3\text{-I}$
- (3) Boiling point: $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$



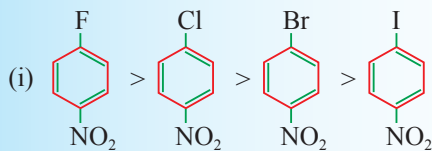
- (4) Density: $n\text{-C}_3\text{H}_7\text{Cl} < n\text{-C}_3\text{H}_7\text{Br} < n\text{-C}_3\text{H}_7\text{I}$
- (5) Solubility \rightarrow slightly soluble in water



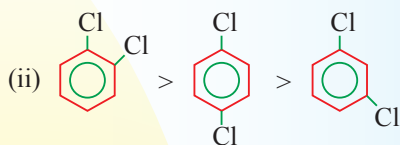
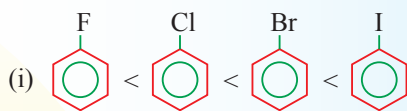
HALO-ARENE



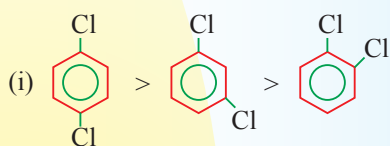
(A) [Reactivity toward Nucleophile]



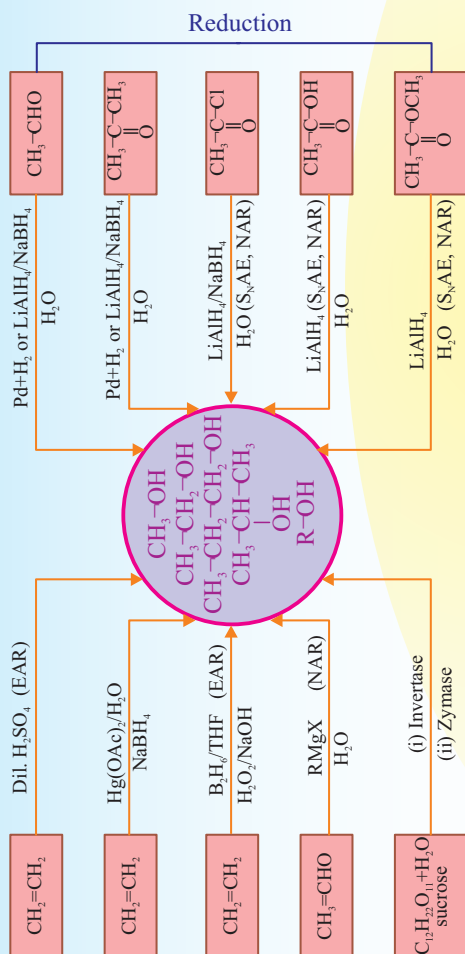
(B) Boiling point



(C) Melting point



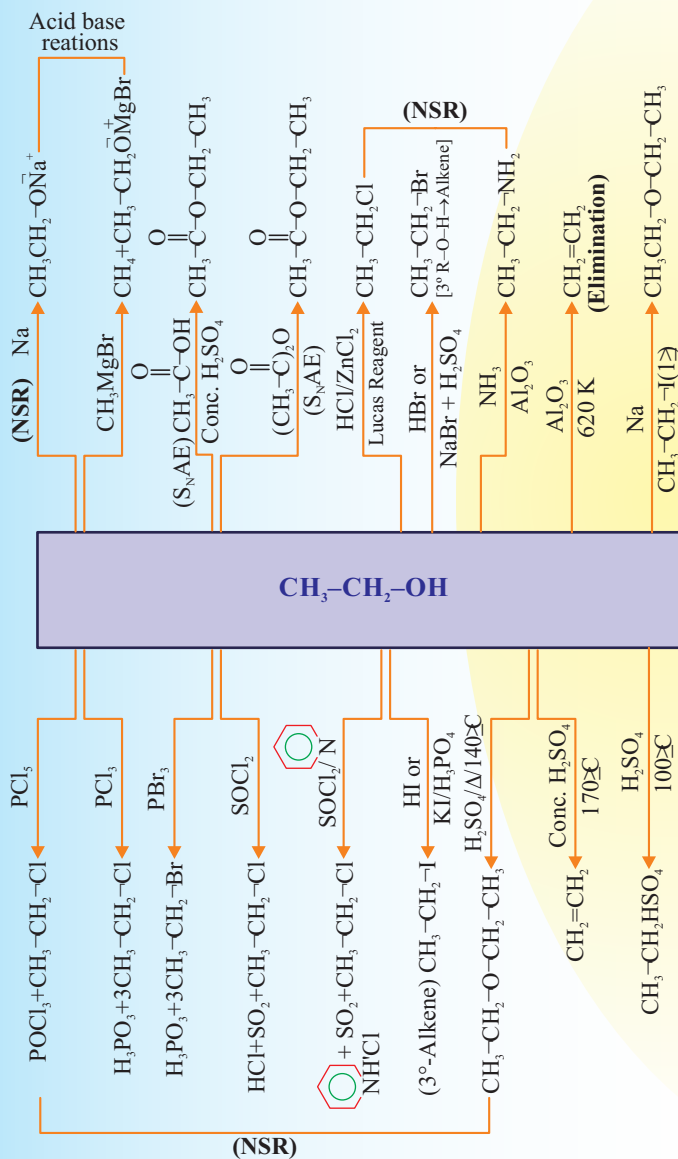
Alcohol, Phenol and Ether



Solubility of alcohol increase in branching $n < \text{iso} < \text{neo}$ (Isomeric).

Relative order of reactivity

- (i) $1^\circ > 2^\circ > 3^\circ$ (O-H bond fission)
- (ii) $3^\circ > 2^\circ > 1^\circ$ (C-O bond fission)
- (iii) $3^\circ > 2^\circ > 1^\circ$ (Dehydration)

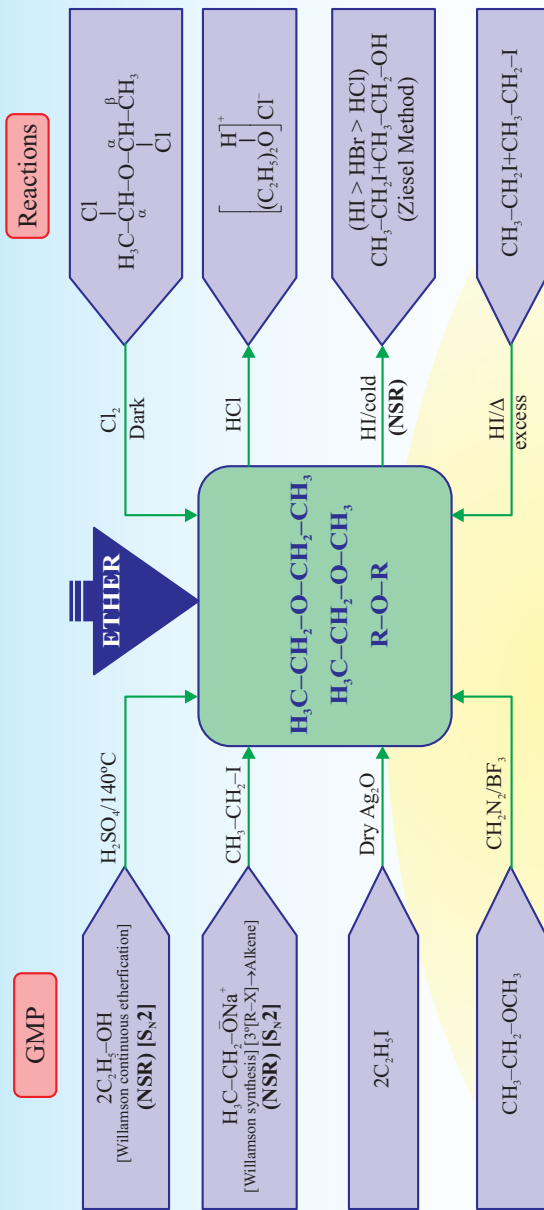


DEHYDROGENATIONS

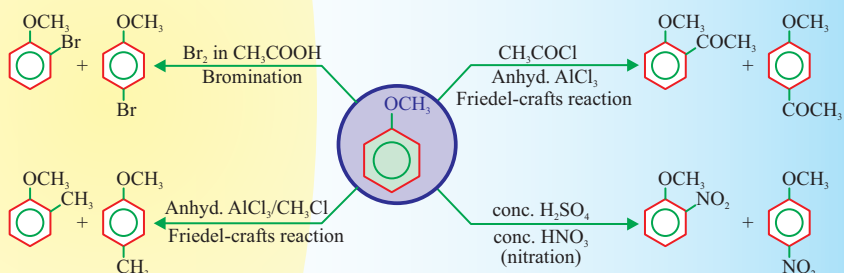
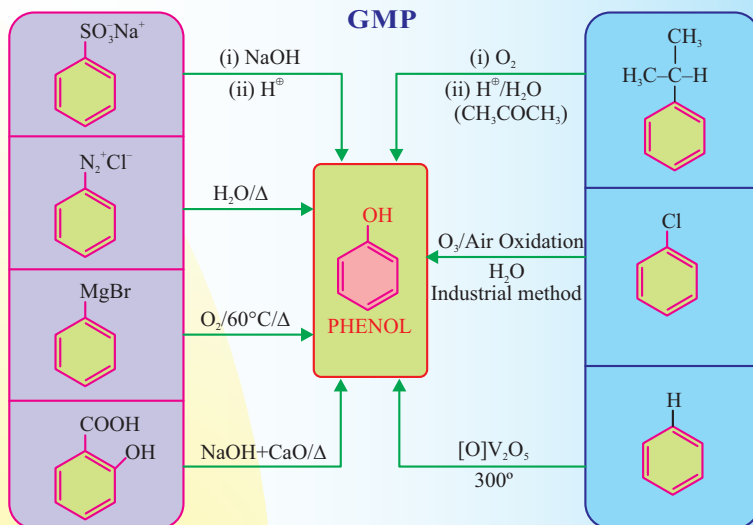
| Reagent | $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{OH}}{\text{CH}_2}$ 1° Alcohol | $\text{H}_3\text{C}-\text{CH}_2-\overset{\text{OH}}{\text{CH}}-\text{CH}_3$ 2° Alcohol | $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{OH}$ 3° Alcohol |
|---|---|--|--|
| PCC/PDC Anhy. CrO_3 | $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{H}$ | $\text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{CH}_3$ | No reaction |
| $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^\oplus$ $\text{KMnO}_4/\text{H}^\oplus$ OH/Δ Jones Reagent | $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{OH}$ | $\text{H}_3\text{C}-\overset{\text{O}}{\text{C}}-\text{OH} + \text{CH}_3-\overset{\text{O}}{\text{C}}-\text{OH}$ | No reaction |
| $\text{Cu}/500^\circ\text{C}$ | $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{H}$ | $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{CH}_3$ | $\text{H}_3\text{C}-\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$ |
| Lucas Reagent HCl/ZnCl_2 | Cloudiness appear upon heating after 30 mins. | within five min. | Immediately |

VICTOR MEYER'S TEST

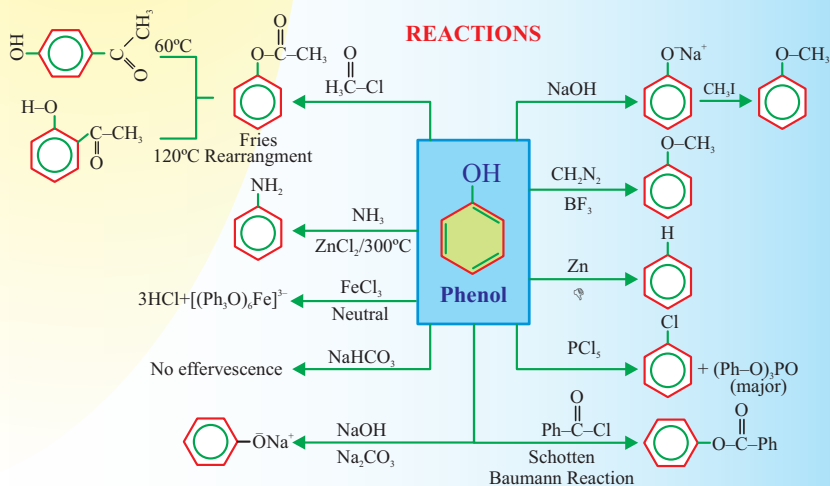
| | | | |
|-----------------------|--|---|---|
| P/I_2 | $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{I}$ | $\text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{I}$ | $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{I}$ |
| AgNO_2 | $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NO}_2$ | $\text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{NO}_2$ | $(\text{CH}_3)_3\text{C}-\text{NO}_2$ |
| HNO_2 | $\text{H}_3\text{C}-\text{CH}_2-\overset{\text{N}-\text{OH}}{\text{C}}-\text{NO}_2$ Nitrolic acid | $\text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{N}=\text{O}}{\text{C}}}-\text{NO}_2$ Blue colour | No reaction: Colourless |
| NaOH | Red Colour | No reaction | |

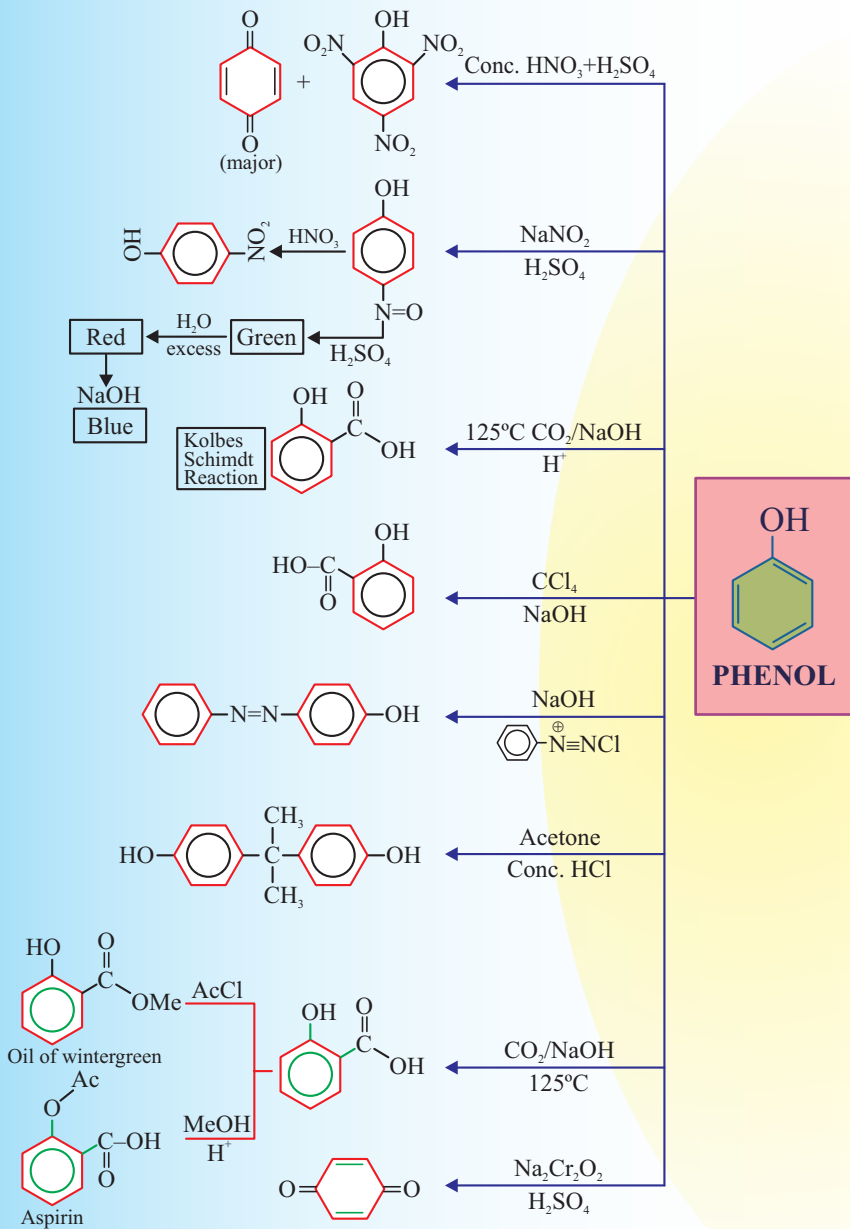


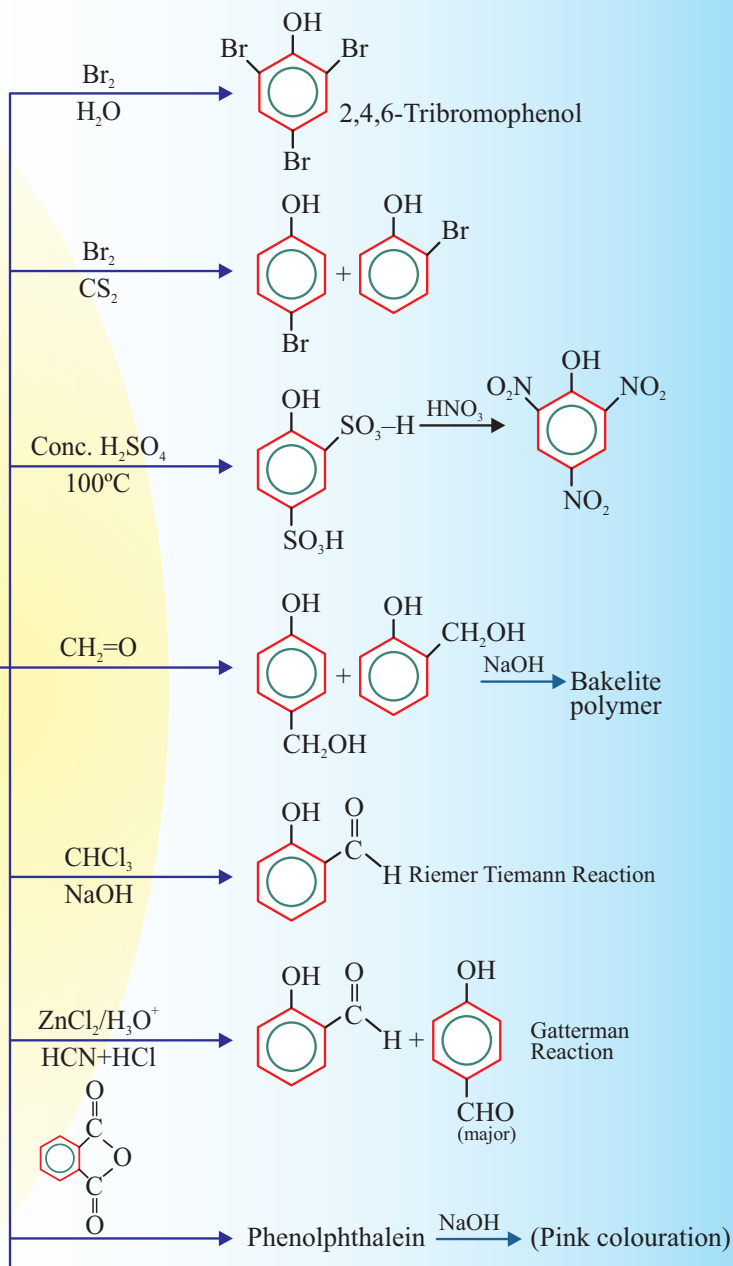
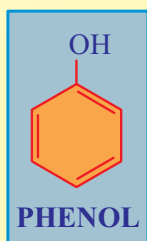
PHENOL GMP



REACTIONS







| Comparison of S _N 1 and S _N 2 | | | |
|---|------------------------|-----------------------|---------------------------|
| Reactions | | S _N 1 | S _N 2 |
| A | Kinetics | 1 st order | 2 nd order |
| B | Rate | k[RX] | k[RX] [Nu: [⊖]] |
| C | Stereochemistry | Racemisation | Inversion |
| D | Substrate (reactivity) | 3° > 2° > 1° > MeX | MeX > 1° > 2° > 3° |
| E | Nucleophile | Rate Independent | Needs Strong Nu |
| F | Solvent | Good ionizing | Faster in aprotic |
| G | Leaving Group | Needs Good LG | Needs Good LG |
| H | Rearrangement | Possible | Not Possible |

| Comparison of E ₁ and E ₂ | | | |
|---|-----------------|-----------------------|--------------------------|
| Reactions | | E ₁ | E ₂ |
| A | Kinetics | 1 st order | 2 nd order |
| B | Rate | k[RX] | k[RX] [B: ⁻] |
| C | Stereochemistry | No special geometry | Anti-periplanar |
| D | Substrate | 3° > 2° >>> 1° | 3° > 2° > 1° |
| E | Base Strength | Rate Independent | Needs Strong bases |
| F | Solvent | Good ionizing | Polarity not import |
| G | Leaving Group | Needs Good LG | Needs Good LG |
| H | Rearrangement | Possible | Not Possible |

| Summary of S _N 1, S _N 2, E ₁ and E ₂ Reactions | | | | |
|--|--------------------|---|---------------|--------|
| RX | Mechanism | Nu/B | Solvent | Temp. |
| 1° | S _N 2 | [⊖] Better OH, C ₂ H ₅ O [⊖] | Polar aprotic | Low |
| | E ₂ | Strong & bulky base (CH ₃) ₃ CO [⊖] | | High |
| 2° | S _N 2 | [⊖] HO, C ₂ H ₅ O [⊖] | Polar aprotic | Low |
| | E ₂ | (CH ₃) ₃ CO [⊖] | | High |
| | (S _N 1) | (Solvent) | Polar aprotic | (Low) |
| | (E ₁) | (Solvent) | | (High) |
| 3° | S _N 1 | Solvent | Protic | Low |
| | E ₁ | Solvent | Protic | High |

| | Primary (1°) | Secondary (2°) | Tertiary (3°) |
|------------------------------|----------------|--|--|
| Strong nucleophile | $S_N2 \gg E_2$ | $S_N2 + E_2$ (if weak base, S_N2 favored) | E_2 |
| Weak nucleophile weak base | Mostly S_N2 | Mostly S_N2/S_N1 | Mostly S_N1 at low T mostly E_1 at high T |
| Weak nucleophile strong base | Mostly E_2 | Mostly E_2 | E_2 |

Order of reactivity of Allylic Halide towards

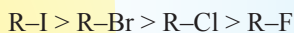
$$S_N1 \propto \text{Benzylic} > \text{Allylic} > 3^\circ > 2^\circ > 1^\circ$$

$$S_N1 \propto \text{Stability of carbocation}$$

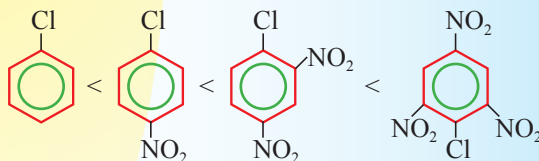
$$S_N2 \propto 1^\circ > 2^\circ > 3^\circ$$

$$S_N2 \propto \frac{1}{\text{Steric hindrance}}$$

Reactivity order towards S_N1 or S_N2 and E_1 or E_2

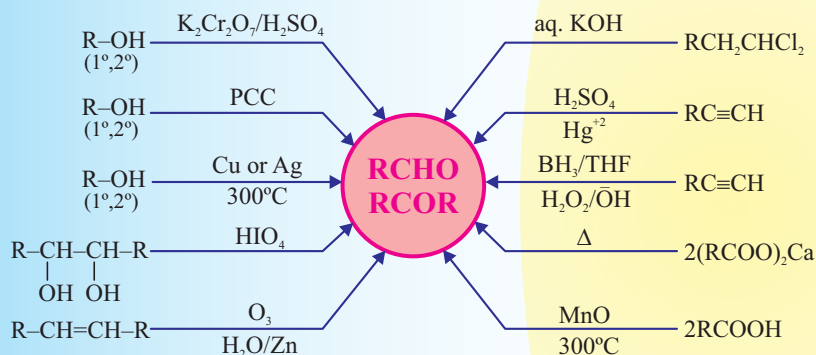


With increase in number of strong electron withdrawing group at ortho and para position, reactivity of X towards aromatic nucleophilic substitution increases.

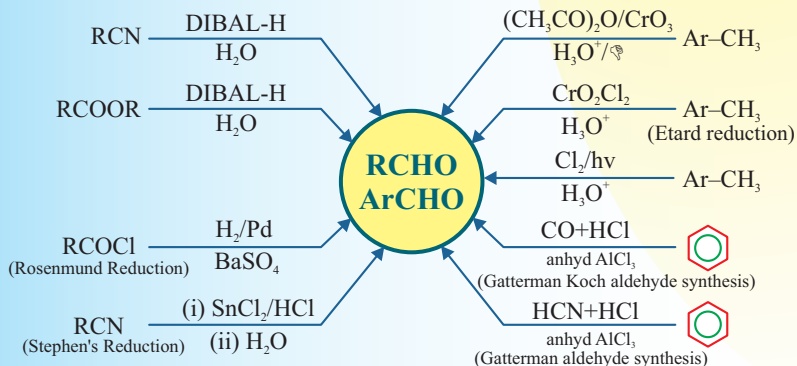


Aldehyde, Ketone and Carboxylic Acid

Preparation of Aldehyde & Ketone both

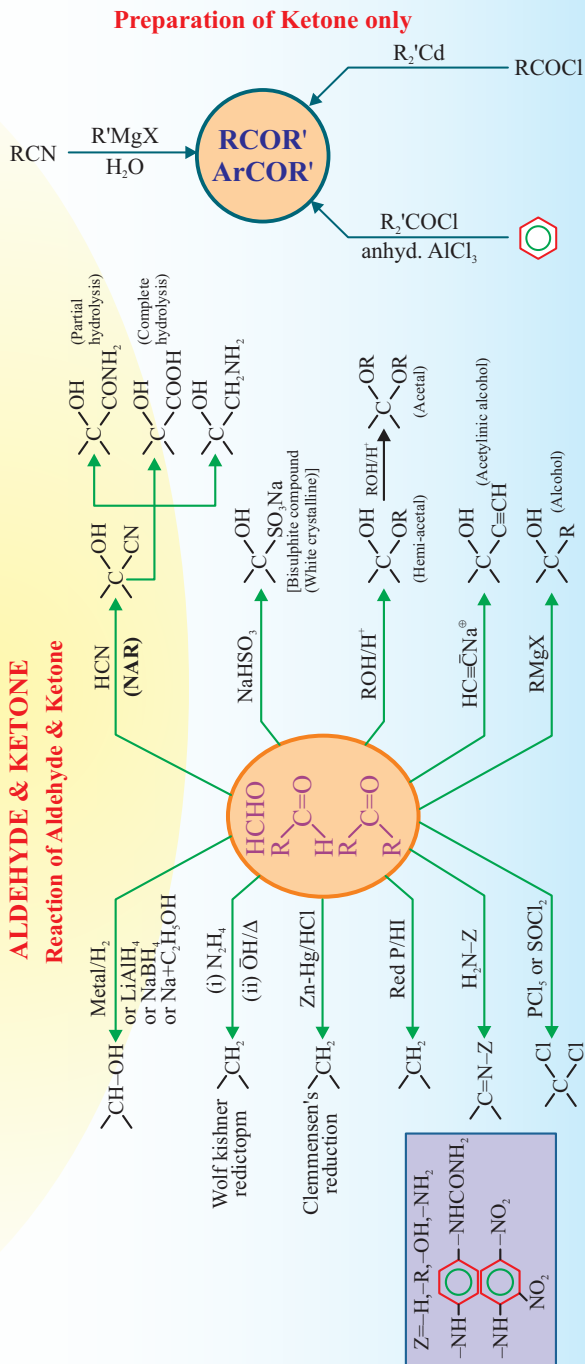


Preparation of Aldehyde only

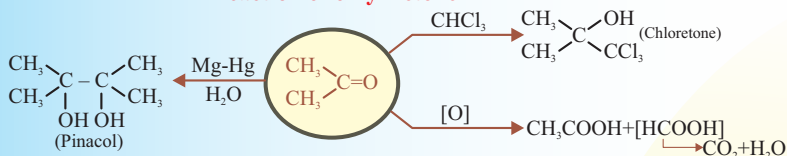


ALDEHYDE & KETONE

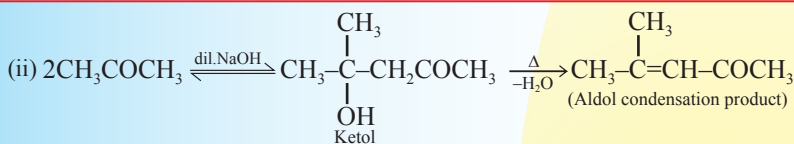
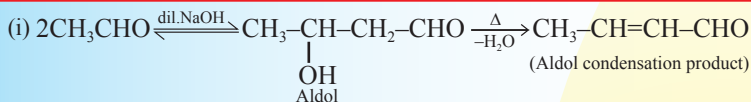
Reaction of Aldehyde & Ketone



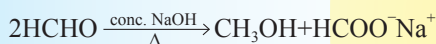
Reaction of only Ketone



Aldol Reaction (Aldehyde or ketone with αH)

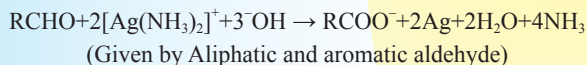


Cannizzaro reaction (Aldehyde with no αH)

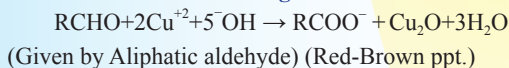


TEST

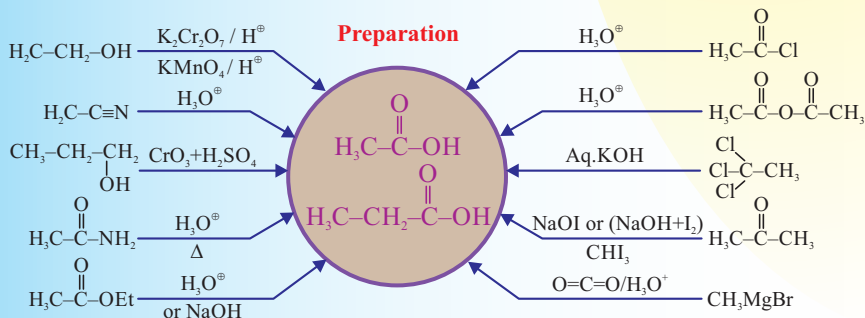
Tollen's test



Fehling's test

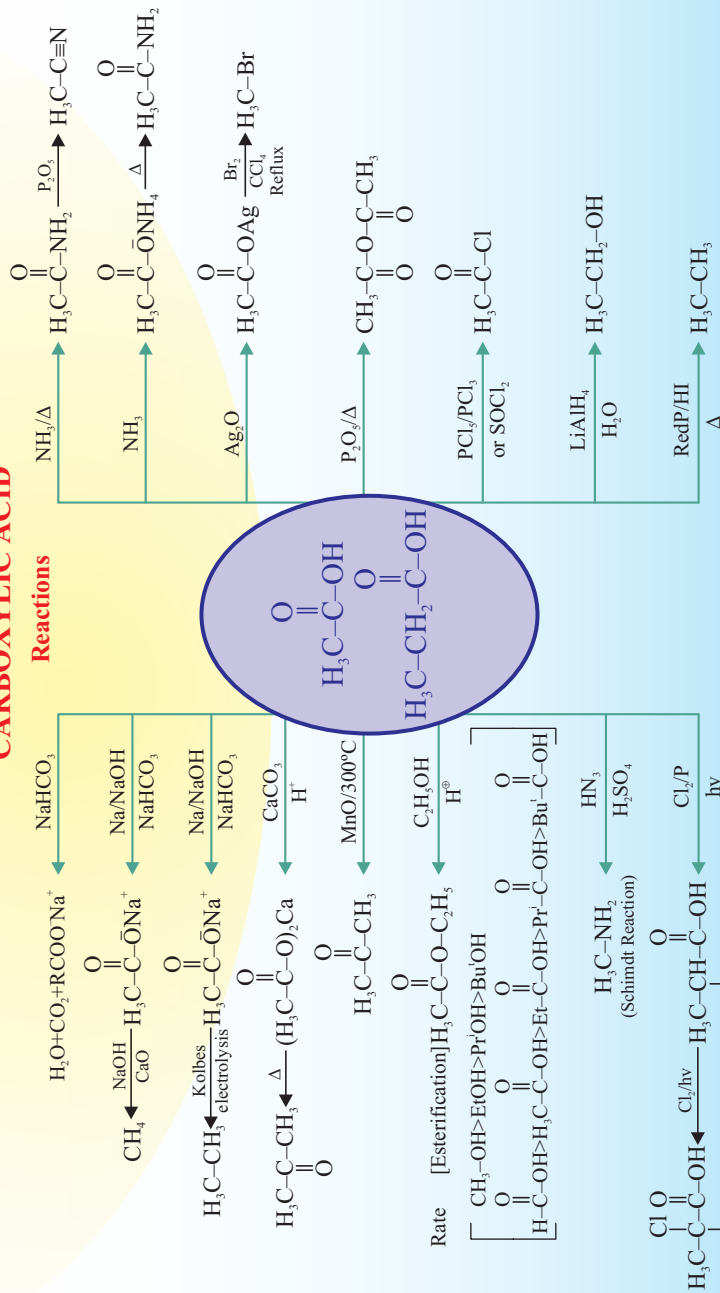


Preparation

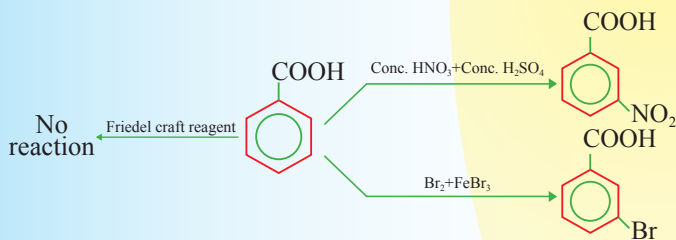
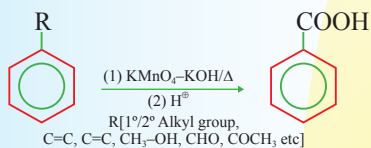


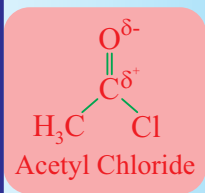
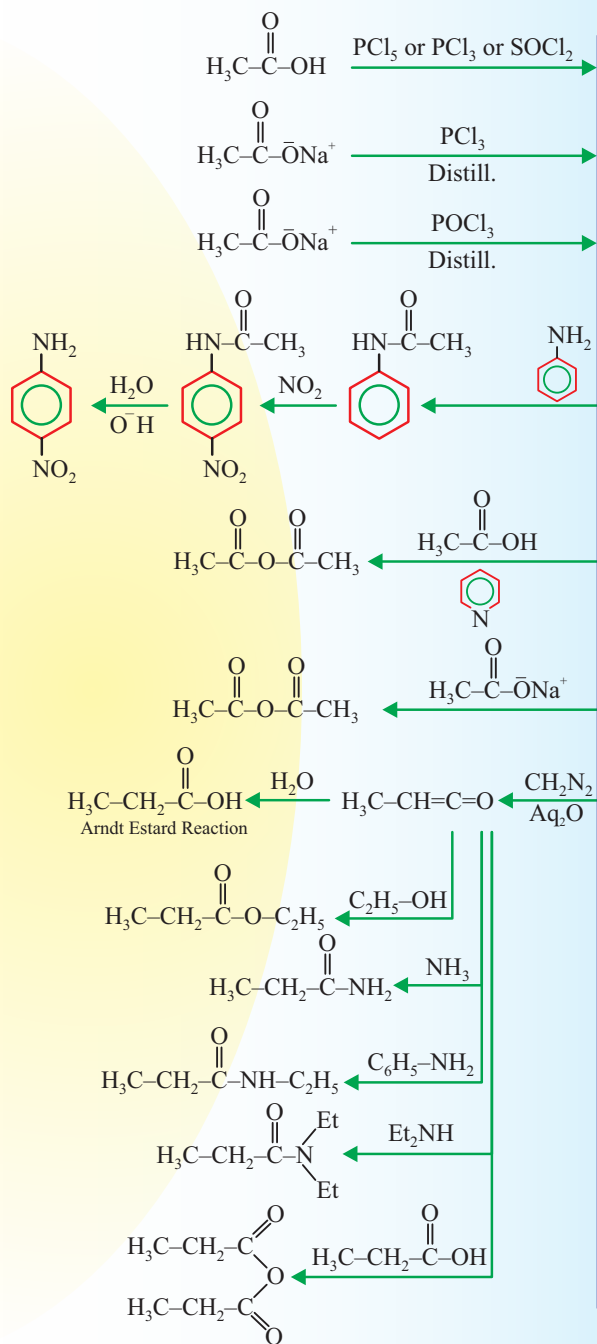
CARBOXYLIC ACID

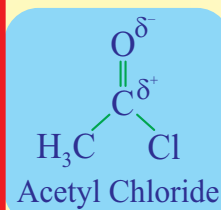
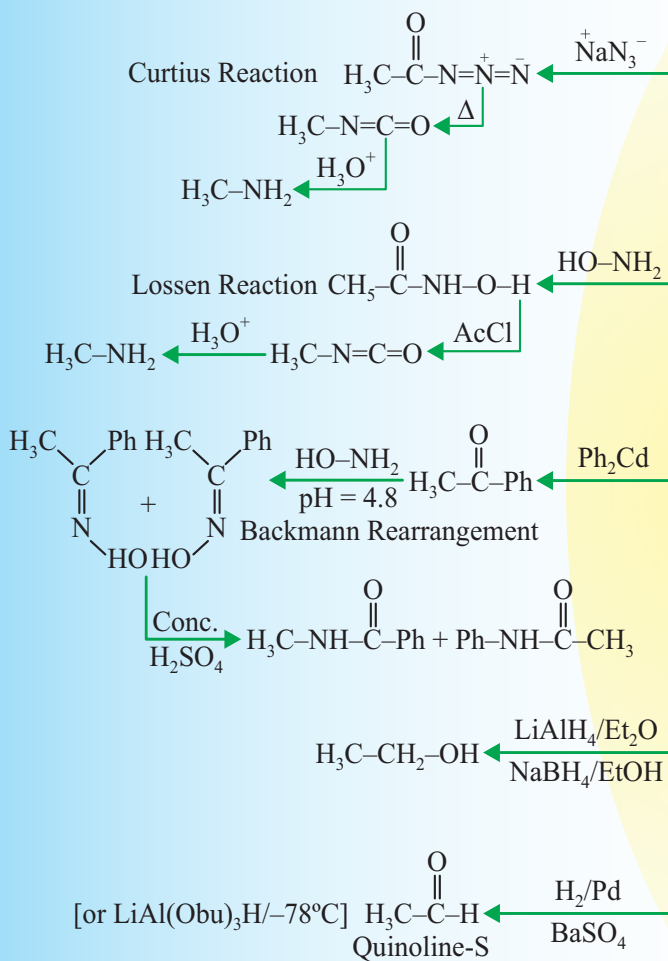
Reactions

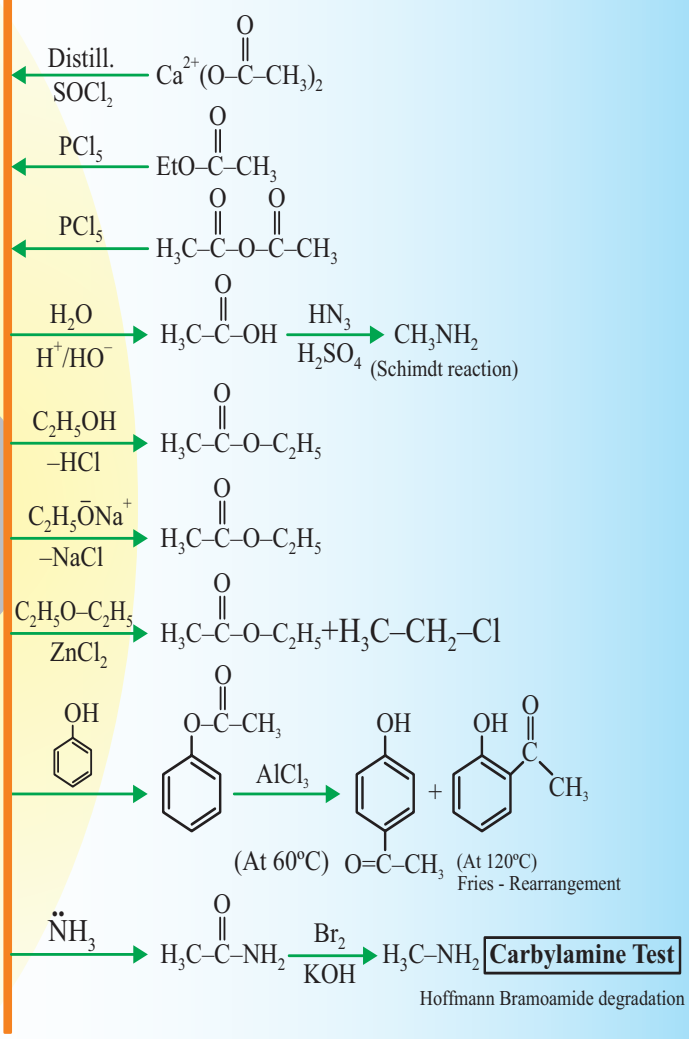
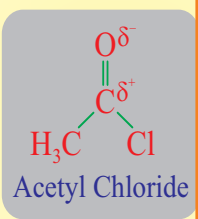


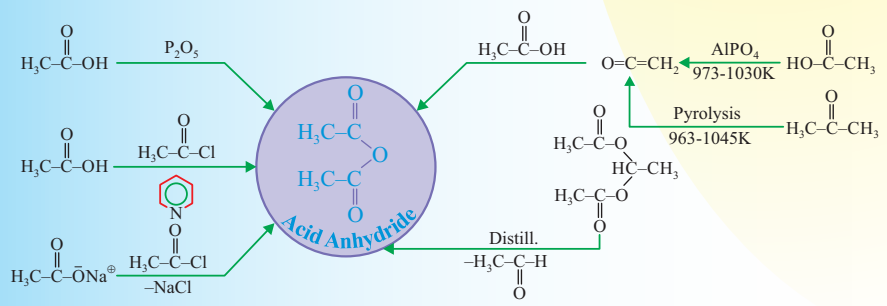
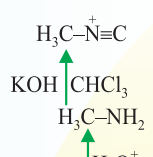
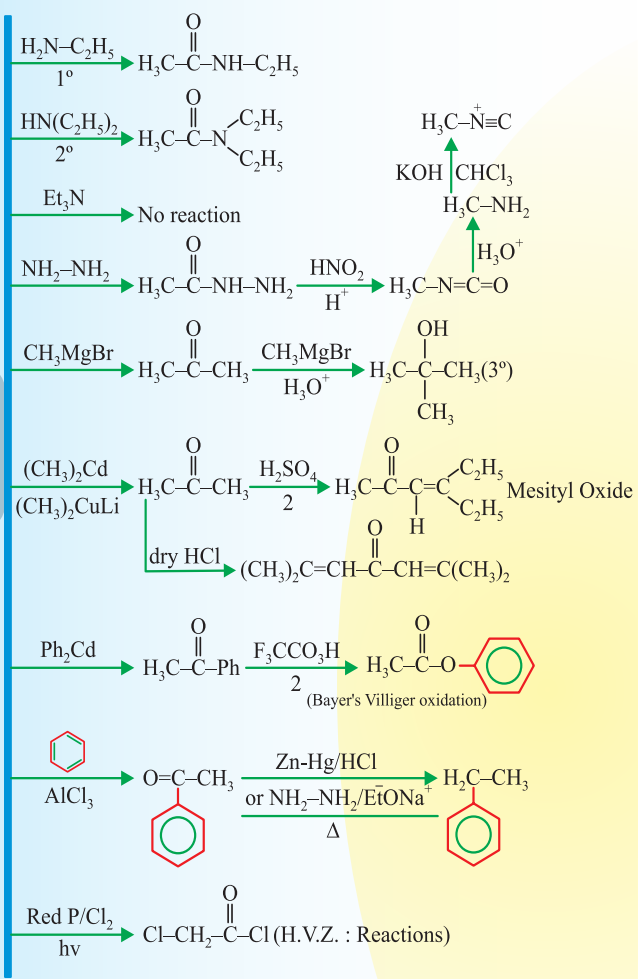
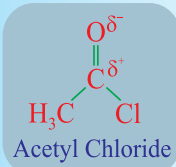
| TEST | |
|---|---|
| Tollen's Reagent | Fehling solution |
| $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \rightarrow \text{Ag}\downarrow + \text{CO}_2\uparrow + \text{H}_2\text{O}$ | $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \xrightarrow{2\text{CuO}} \text{Cu}_2\text{O}\downarrow + \text{CO}_2 + \text{H}_2\text{O}$ <p style="text-align: center;">red ppt.</p> |

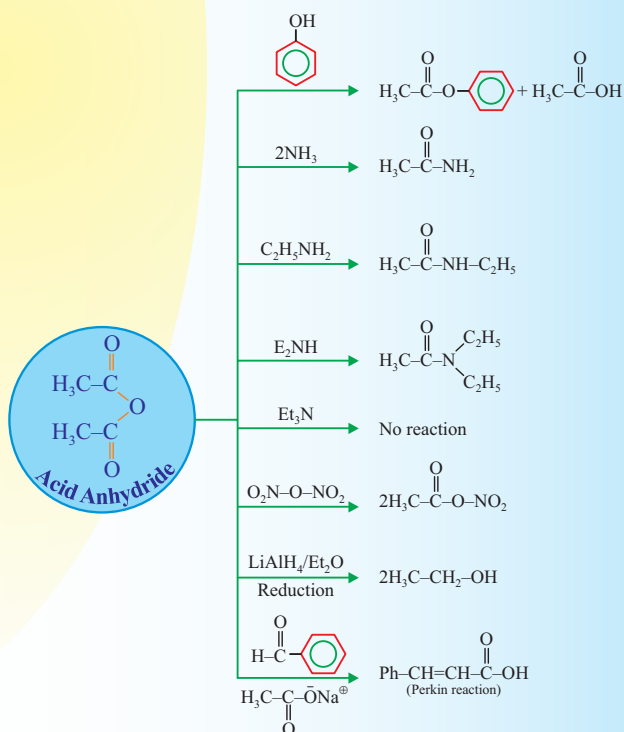
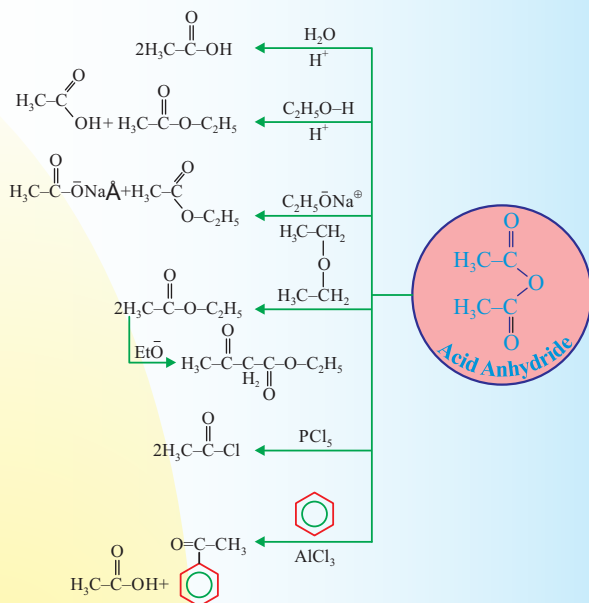




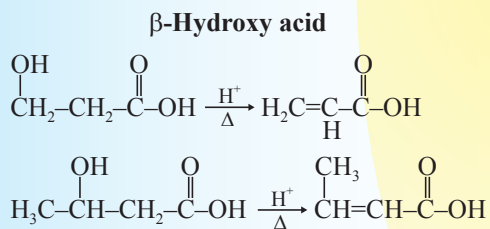
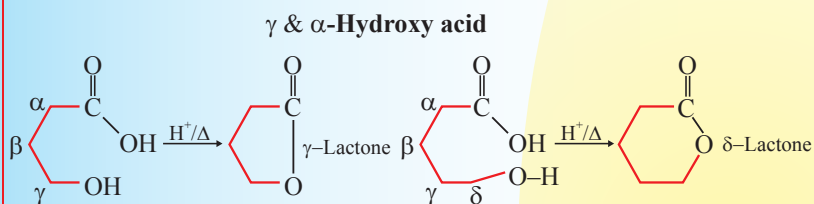
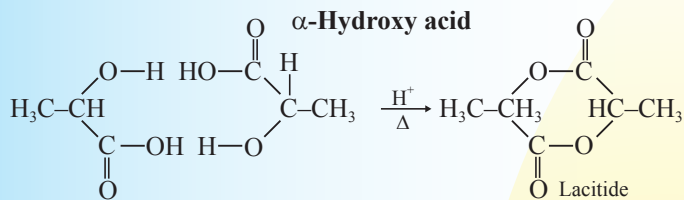




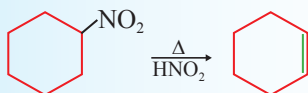
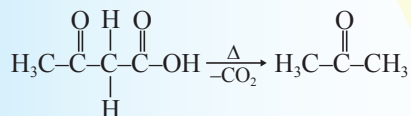




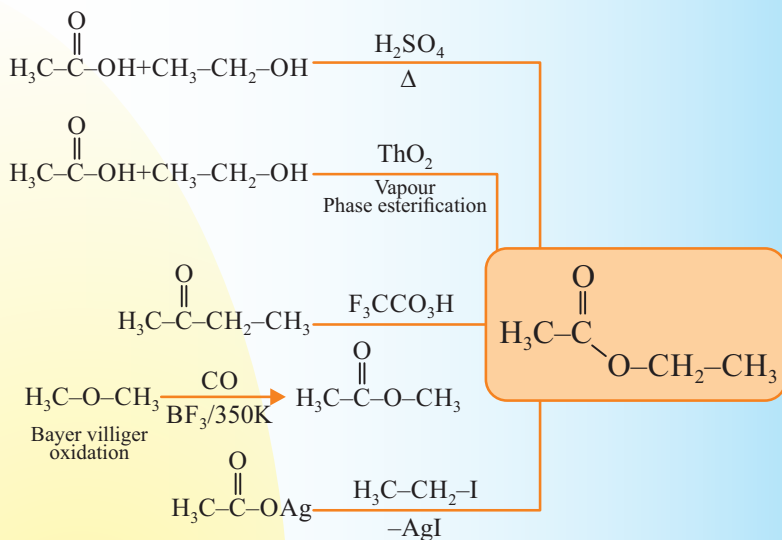
Heating Effect



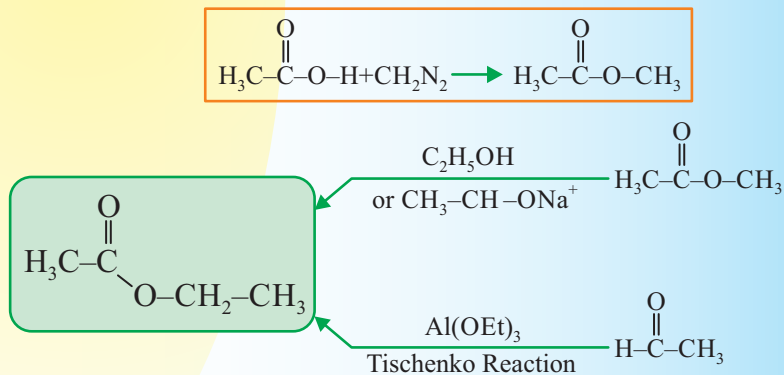
β -Keto acid



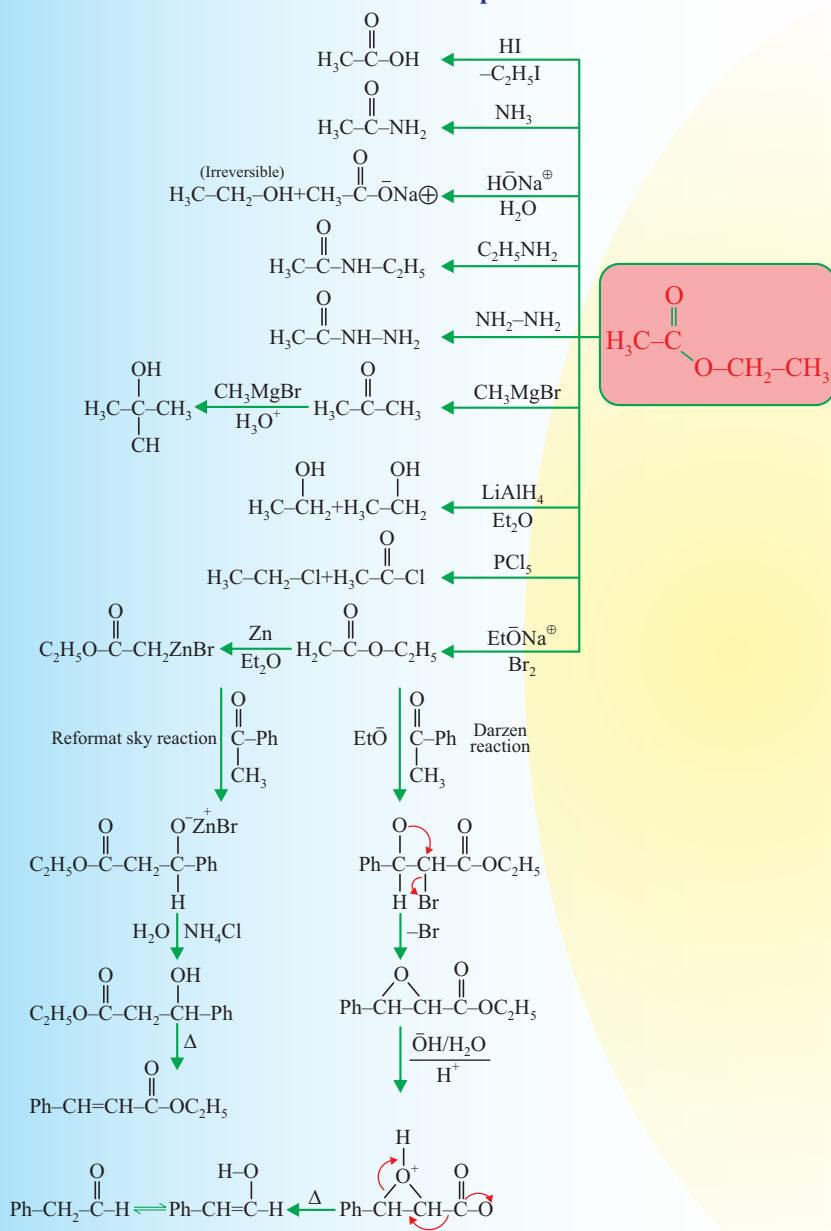
Nutshell preparation of Ester



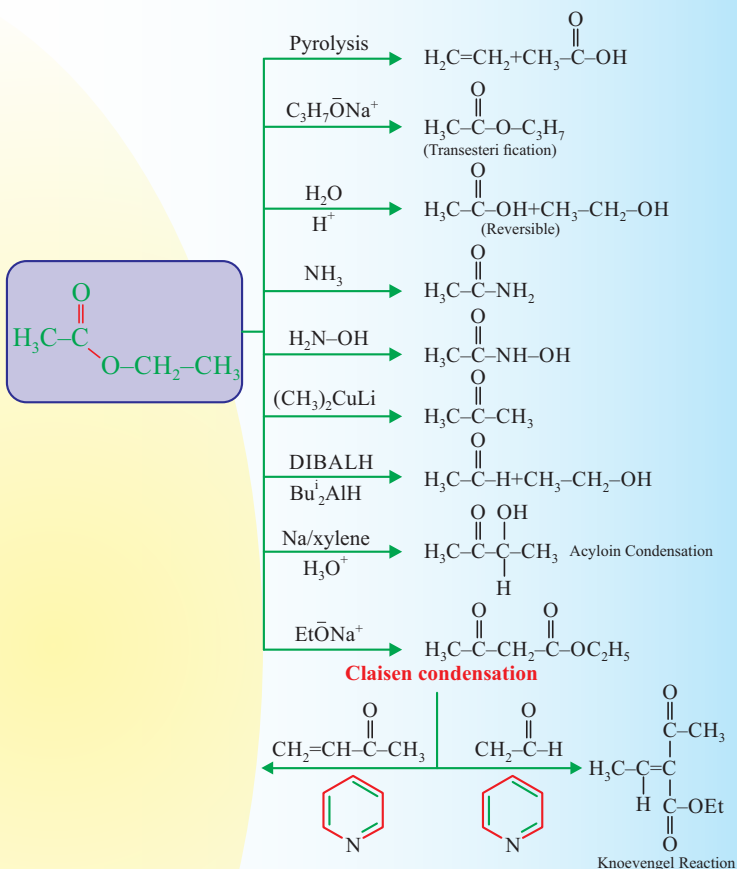
Nutshell preparation of Ester



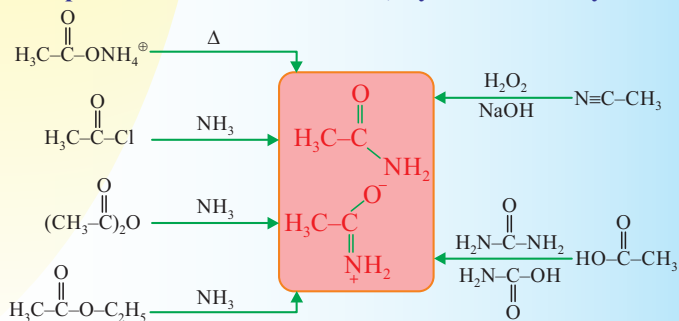
Nutshell Chemical Properties of Ester



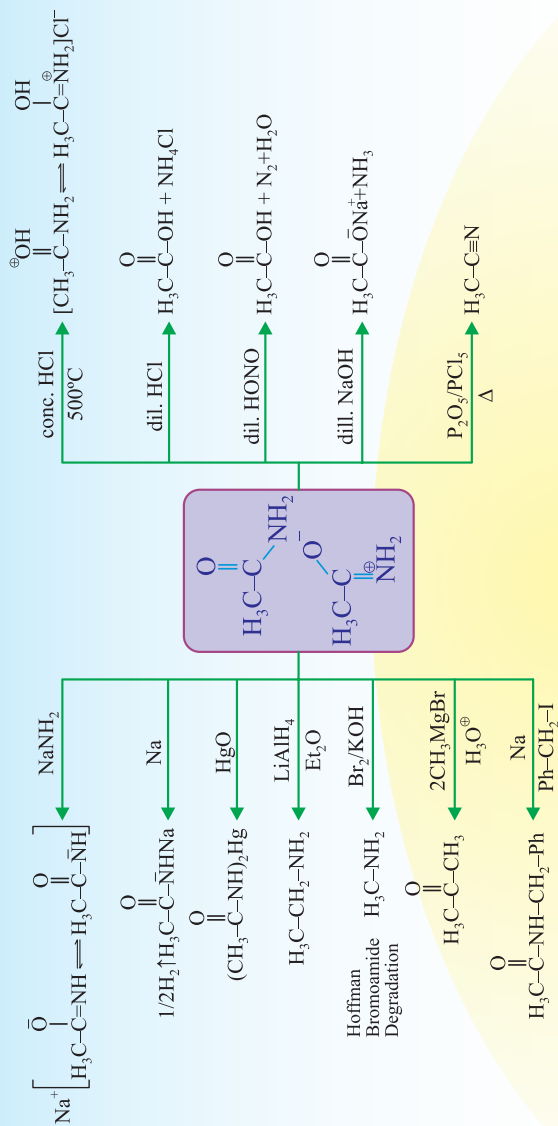
Nutshell Chemical Properties of Ester



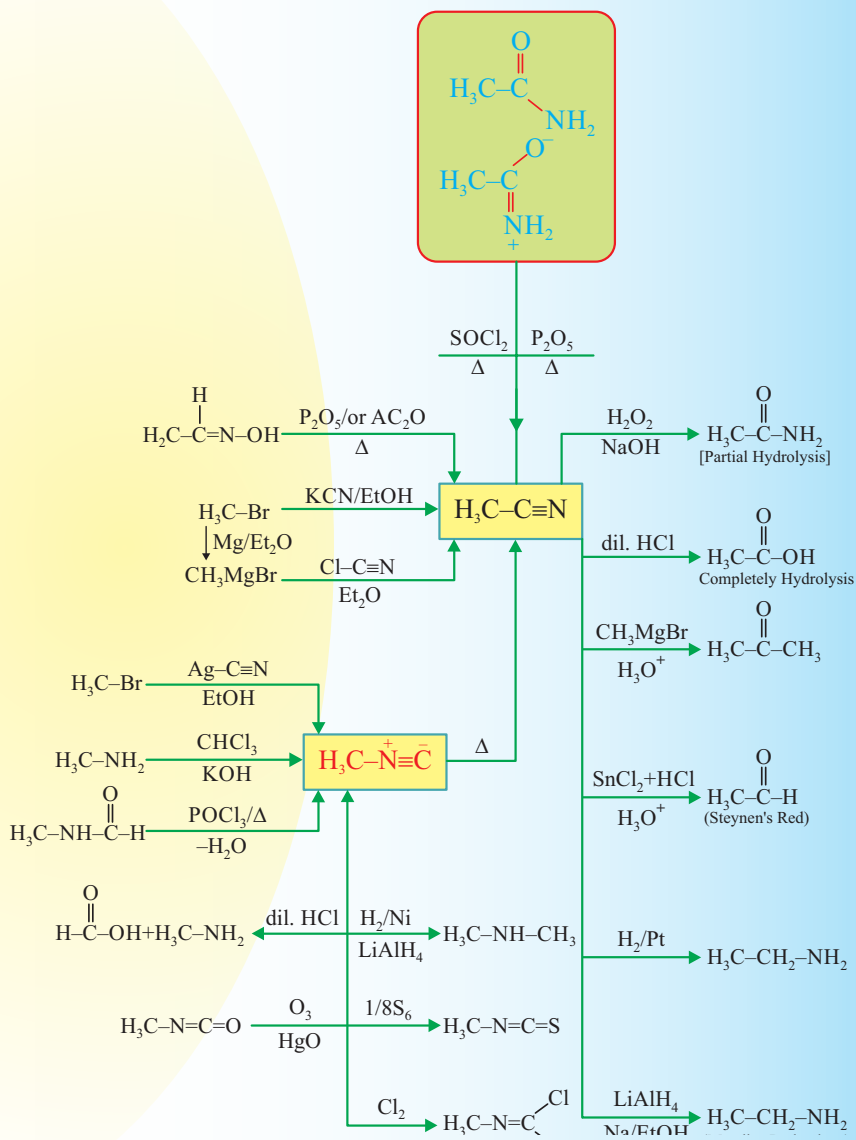
Nutshell preview and review of Amide, Cyanide and Isocyanide



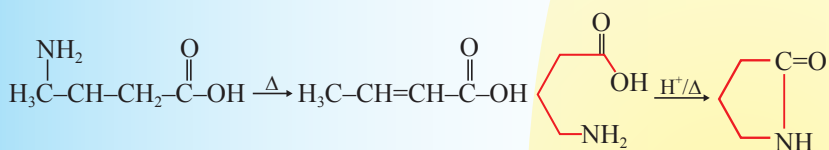
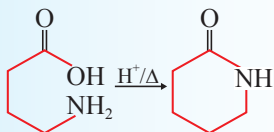
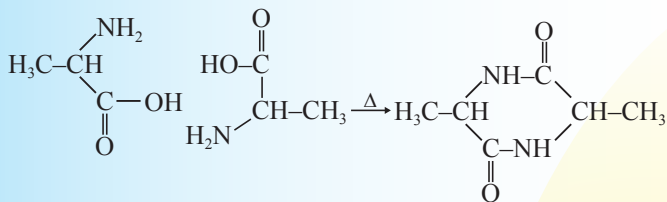
Nutshell preview and review of Amide, Cyanide and Isocyanide



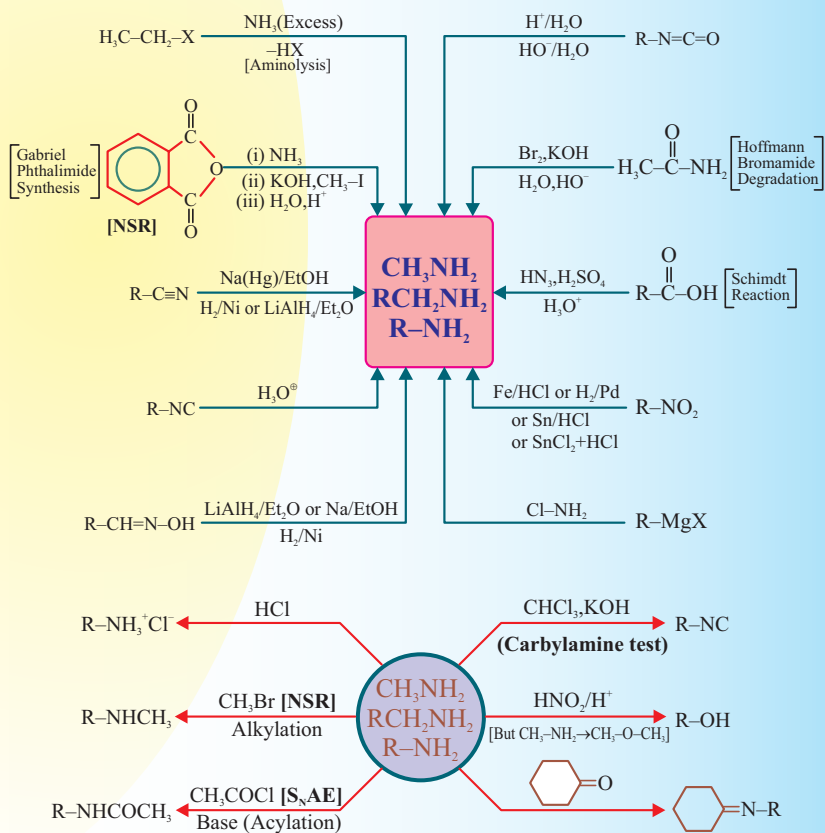
Nutshell preview and review of Amide, Cyanide and Isocyanide

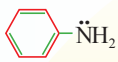
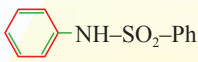


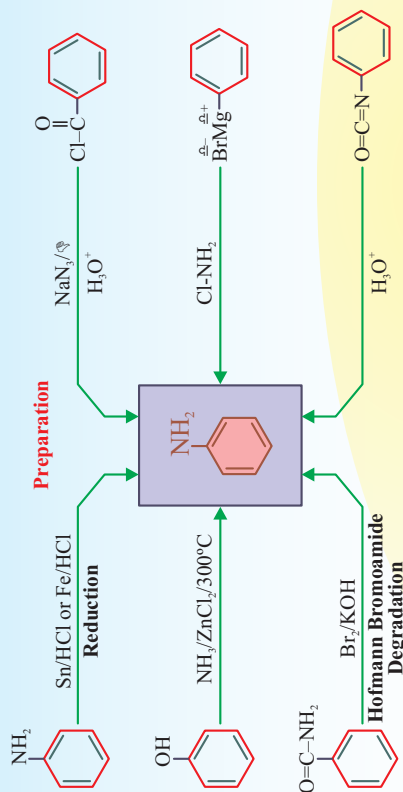
Amino Acid:



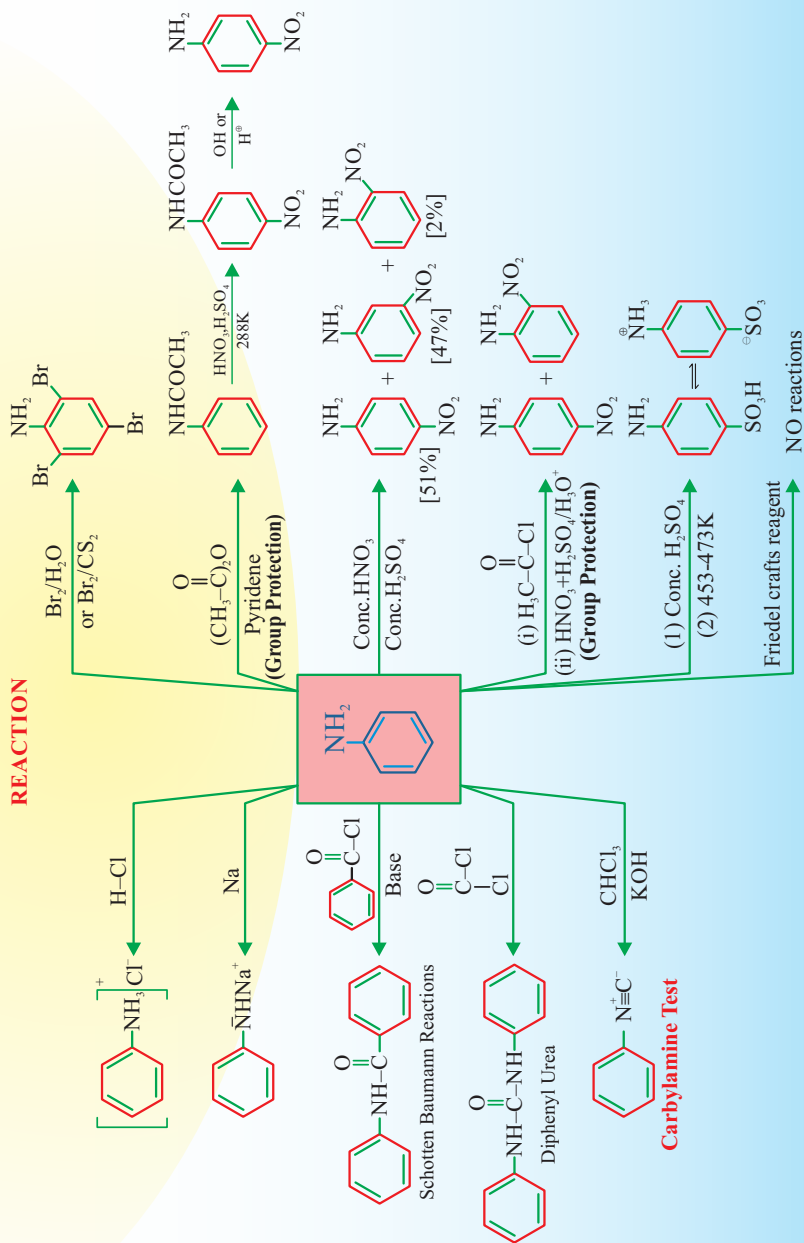
Amines

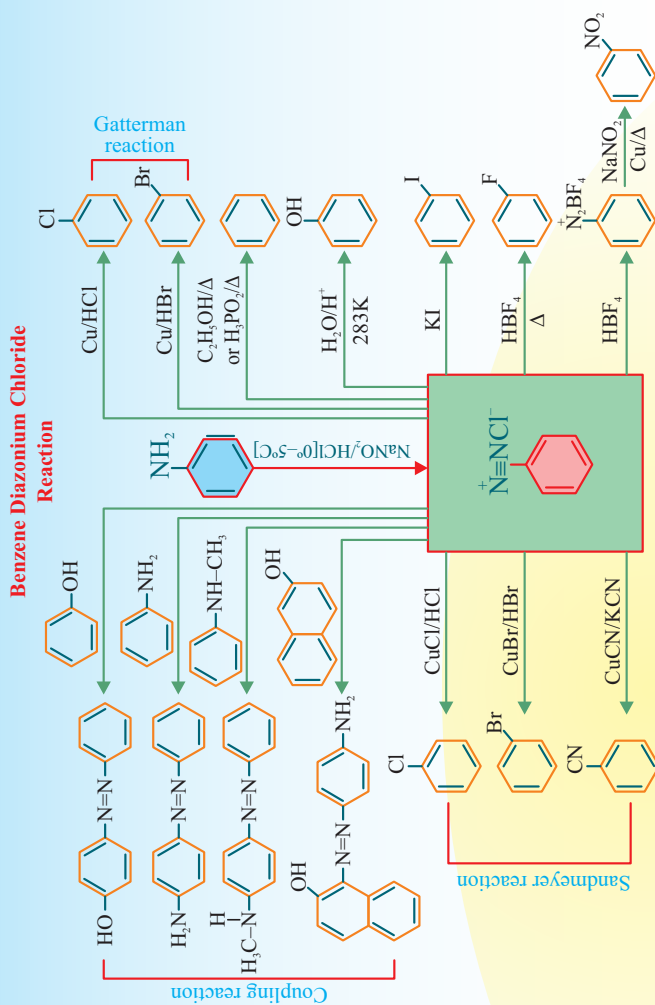


| Test | | | | |
|---|---|--|------------------------|---|
| Reagent | $R-\ddot{N}H_2(1^\circ)$ | $R_2\ddot{N}H(2^\circ)$ | $R_3\ddot{N}(3^\circ)$ |  |
| $Ph-SO_2Cl$ (Hinsberg reagent) | $\begin{array}{c} R-N-SO_2-Ph \\ \\ H \\ \downarrow NaOH \\ [R-\overset{\ominus}{N}-SO_2-Ph]Na^+ \end{array}$ soluble | $\begin{array}{c} O \\ \\ R_2N-S-Ph \\ \\ O \\ \downarrow NaOH \\ Insoluble \end{array}$ | No reaction |  |
| $\begin{array}{c} S \\ \\ C=S \\ \Delta/HgCl_2 \\ \text{Mustard oil test} \end{array}$ | $\begin{array}{c} S \\ \\ R-NH-C-SH \\ \downarrow HgCl_2, \Delta \\ R-N=C=S+HgS \end{array}$ | $\begin{array}{c} S \\ \\ R_2N-C-SH \\ \downarrow HgCl_2, \Delta \\ \text{No reaction} \end{array}$ | No reaction | $\xrightarrow{KOH} Ph-N=C=S+HgS$ |



REACTION



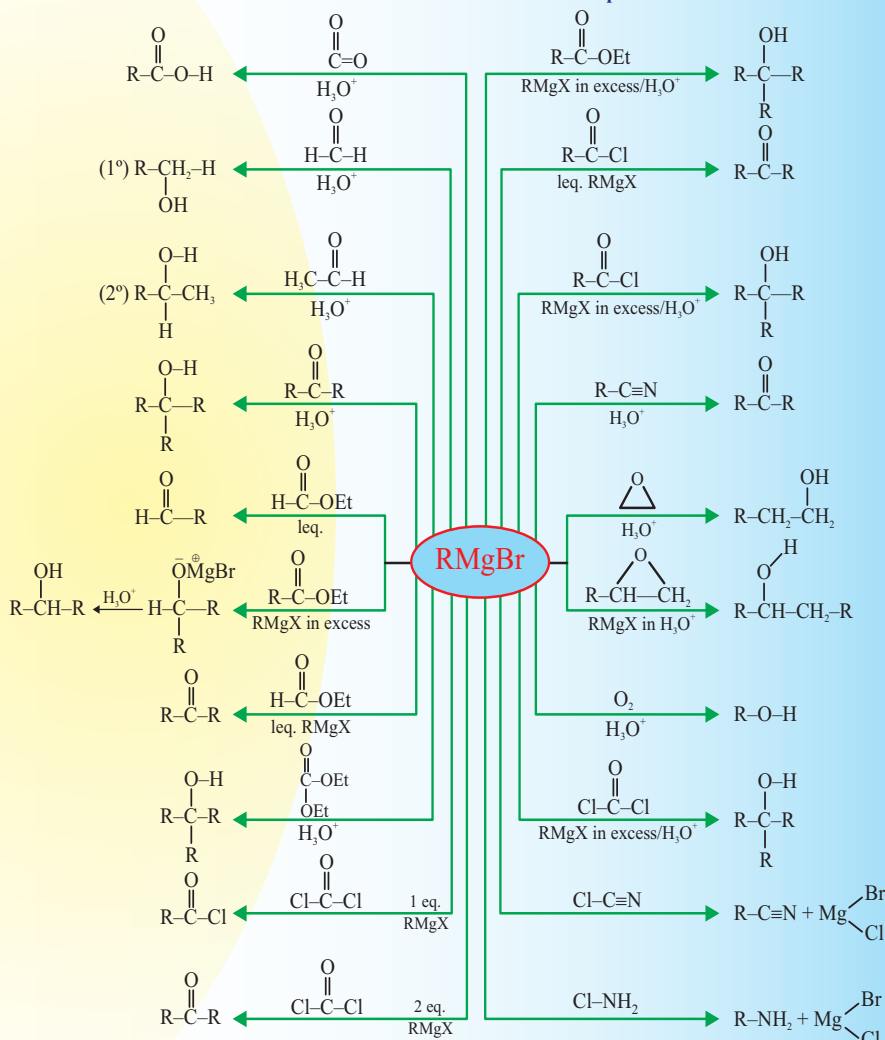


| | |
|-------------------|--|
| FrSR | Free Radical Substitution reaction |
| ESR | Electrophilic Substitution reaction |
| NSR | Nucleophilic Substitution reaction |
| S _N AE | Substitution Nucleophilic (addition elimination) |
| FrAR | Free radical addition reaction |
| NAR | Nucleophilic addition reaction |
| EAR | Electrophilic addition reaction |
| FrER | Free Radical Elimination reaction |

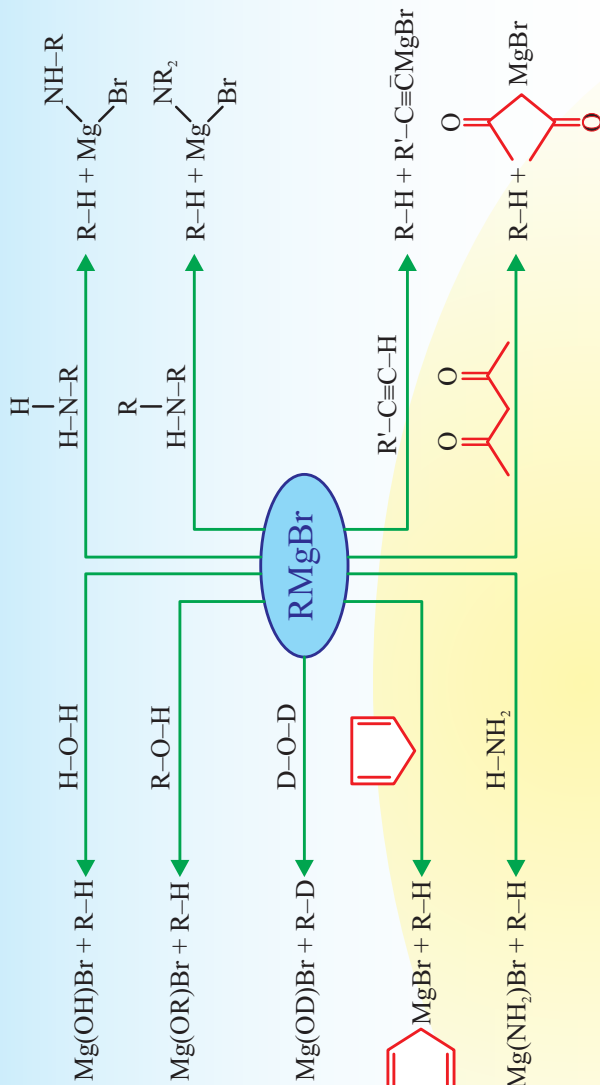
GRIGNARD REAGENT

REACTION

GRIGNARD REAGENT as Nucleophile



GRIGNARD REAGENT as Base
(Active H-containing compound)



Polymers

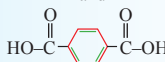
| ADDITION POLYMERS | | | |
|---------------------------|--|--|---|
| S.No | Name of Polymer | Starting Materials | Nature of Polymer |
| I. Polyolefins | | | |
| 1. | Polyethylene or Polyethene | $\text{CH}_2=\text{CH}_2$ | Low density homopolymer (branched chain growth) |
| 2. | Polypropylene or Polypropene | $\text{CH}_3\text{CH}=\text{CH}_2$ | Homopolymer, linear, chain growth |
| 3. | Polystyrene | $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ | Homopolymer, linear, chain growth |
| II. Polydienes | | | |
| 1. | Neoprene | $\begin{array}{c} \text{Cl} \\ \\ \text{CH}_2=\text{CH}-\text{C}=\text{CH}_2 \end{array}$ Chloroprene or 1-Chloro-1,3-butadiene | Homopolymer, chain growth |
| 2. | Buna S (Styrene-Butadiene, Rubber SBR or GRS) | $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ and $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ <small>1,3-butadiene</small> <small>Styrene</small> | Copolymer, chain growth |
| III. Polyacrylates | | | |
| 1. | Polymethylmethacrylate (Flexiglass Lucite, Acrylite or Perspex PMMA) | $\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C}-\text{COOCH}_3 \end{array}$ | Homopolymer |
| 2. | Polyethylacrylate | $\text{H}_2\text{C}=\text{CH}-\text{COOC}_2\text{H}_5$ | Homopolymer |
| 3. | Polyacrylonitrile or Orlon PAN | $\text{CH}_2=\text{CH}-\text{CN}$ | Homopolymer |


| IV. Polyhalofins | | | |
|------------------|--|-----------------------------------|---------------------------|
| 1. | Polyvinyl chloride PVC | $\text{CH}_2=\text{CH}-\text{Cl}$ | Homopolymer, chain growth |
| 2. | Polytetrafluoroethylene or Teflon PTFE | $\text{F}_2\text{C}=\text{CF}_2$ | Homopolymer |
| 3. | Polymonochlorotrifluoroethylene PCTFE | $\text{ClFC}=\text{CF}_2$ | Homopolymer |

CONDENSATION POLYMERS

| S.No | Name of Polymer | Starting Materials | Nature of Polymer |
|------|-----------------|--------------------|-------------------|
|------|-----------------|--------------------|-------------------|

I. Polyesters


| | | | |
|----|--------------------|--|--------------------------------|
| 1. | Terylene or Dacron | $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ Ethylene glycol or Ethane-1,2-diol and  Terephthalic acid or Benzene-1,4-dicarboxylic acid | Copolymer, step growth, linear |
|----|--------------------|--|--------------------------------|

| | | | |
|----|------------------------|---|-------------------------------|
| 2. | Glyptal or Alkyl resin | $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ Ethylene glycol and  Phthalic acid or Benzene-1,2-dicarboxylic acid | Copolymer, linear step growth |
|----|------------------------|---|-------------------------------|

II. Polyamides

| | | | |
|----|-----------|--|--------------------------------|
| 1. | Nylon-6,6 | $\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ Adipic acid and $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$ Hexamethylenediamine | Copolymer, linear, step growth |
|----|-----------|--|--------------------------------|

| | | | |
|----|------------|---|--------------------------------|
| 2. | Nylon-6,10 | $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ Hexamethylene diamine and $\text{HOOC}(\text{CH}_2)_8\text{COOH}$ Sebacic acid | Copolymer, linear, step growth |
|----|------------|---|--------------------------------|

| | | | |
|----|---------|--|---------------------|
| 3. | Nylon-6 |  Caprolactam | Homopolymer, linear |
|----|---------|--|---------------------|

Formaldehyde resins

| | | | |
|----|--------------------------------------|---------------------------|------------------------|
| 1. | Phenolformaldehyde resin or Bakelite | Phenol and formaldehyde | Copolymer, step growth |
| 2. | Melamine formaldehyde resin | Melamine and formaldehyde | Copolymer, step growth |



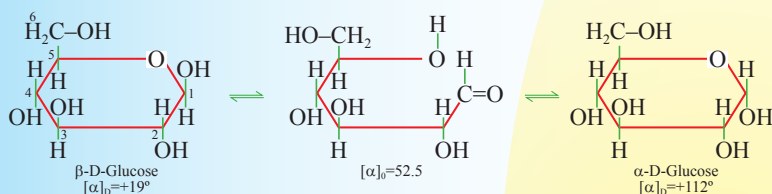
Biomolecules

- Carbohydrates are defined as optically active polyhydroxy aldehydes or ketones or the compound which produce such units on hydrolysis.
- Monosaccharide ($C_nH_{2n}O_n$):** Single unit, can't be hydrolysed : Glucose and fructose.
- Oligosaccharides** gives two to ten monosaccharides on hydrolysis.
- Disaccharides** (by glycosidic linkage)
 - Sucrose $\xrightarrow{H_3O^+}$ α -D. Glucose + β -D. Fructose;
 - Maltose $\xrightarrow{H_3O^+}$ 2 α -D. Glucose unit
 - Lactose $\xrightarrow{H_3O^+}$ β -D. Glucose + β -D. Galactose.
- Polysaccharide:** Contain more than ten monosaccharide units.
 $(C_6H_{10}O_5)_n$: Starch & cellulose.

| TYPE OF SUGAR | | |
|------------------|---|----------------------------|
| Give Test | Reducing | Non Reducing |
| Tollen's Reagent | +ve test | -ve test |
| Fehling Reagent | +ve test | -ve test |
| Benedict Test | +ve test | -ve test |
| Mutarotation | Yes | No |
| Functional Unit | $\begin{array}{c} \alpha \\ \\ -C-C=O \\ \\ OH \end{array} / \begin{array}{c} O \\ \\ -C-C-C- \\ \\ OH \end{array}$ <p>Hemiacetal</p> <p>Hemiketal</p> | <p>Acetal</p> <p>Ketal</p> |

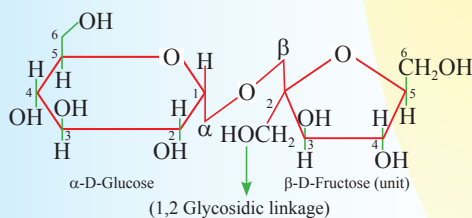
| TYPE OF SUGAR | | |
|---------------|--|--|
| Example | All monosaccharides Glucose Fructose Mannose Galactose | Disaccharide Sucrose Polysaccharide Starch Cellulose |
| | Disaccharide Maltose Lactose | |

- Mutarotation:** When either form of D-glucose is placed in aq. solution it slowly form the other via open chain aldehyde and gradual change in specific rotation until specific rotation ($\pm 52.5^\circ$) is reached.

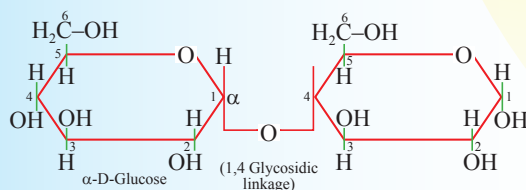


- Anomer's:** Differ in configuration at 1st carbon due to hemi (acetal or ketal) ring formation. The new-asymmetric carbon is referred to as Anomeric carbon.
- Epimer's:** Diastereomer's which differ in conformation at any one chiral carbon.
 eg. D-Glucose & D-mannose
 D-Glucose & D-Galactose

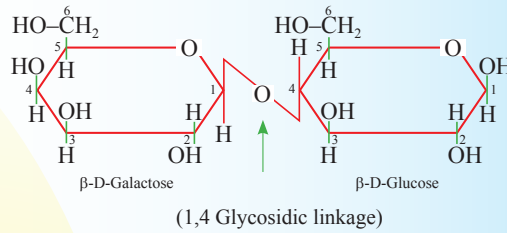
- Sucrose:**



- Maltose:**

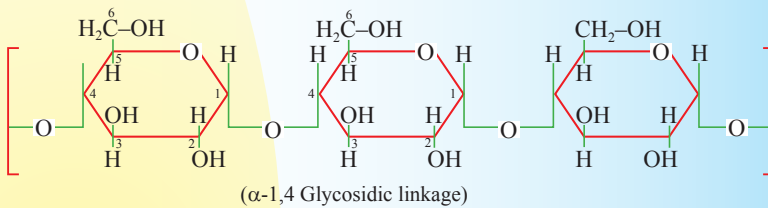


• **Lactose**



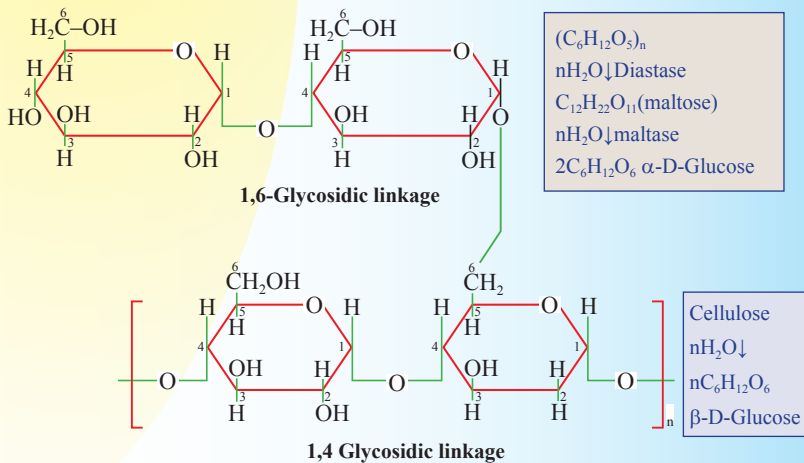
Starch: (Amylose & Amylopectin)

• **Amylose (Straight Chain)**

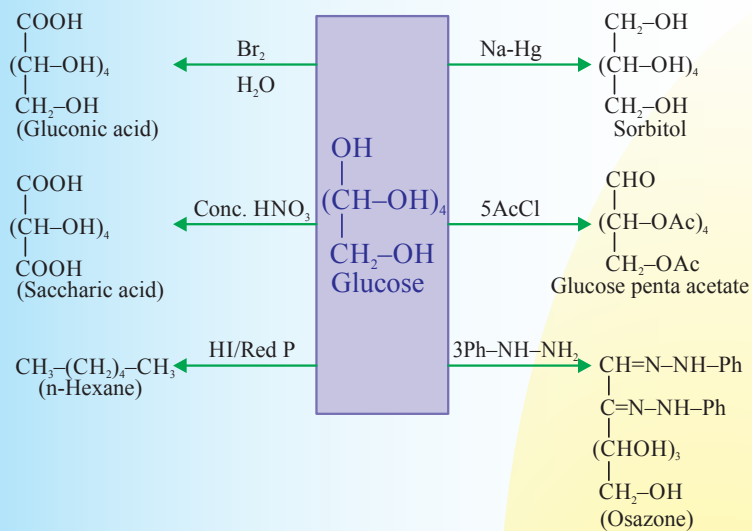


(i) Soluble in H_2O & gives blue colour with I_2

• **Amylopectin (Branch chain): ($C_6H_{12}O_5$)_n**



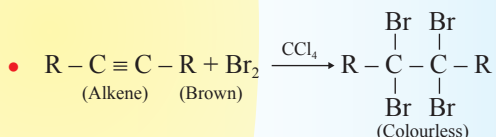
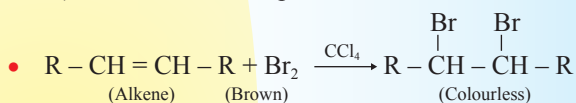
REACTION OF GLUCOSE (OPEN CHAIN STRUCTURE)



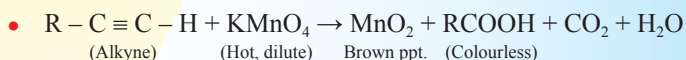
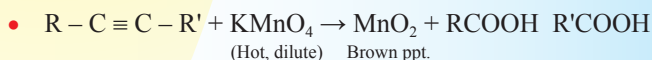
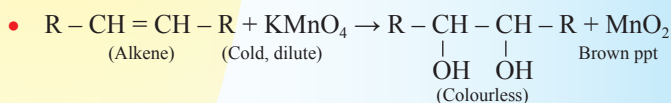
Distinction between Pairs of Compounds

UNSATURATION TEST

(a) Double/Triple bonded Compounds (C=C)/(C≡C) + Br₂ in CCl₄ (Brown colour) → Colourless compound.



(b) Double/Triple bonded Compounds + Baeyer's reagent (Pink colour) → Brown precipitate



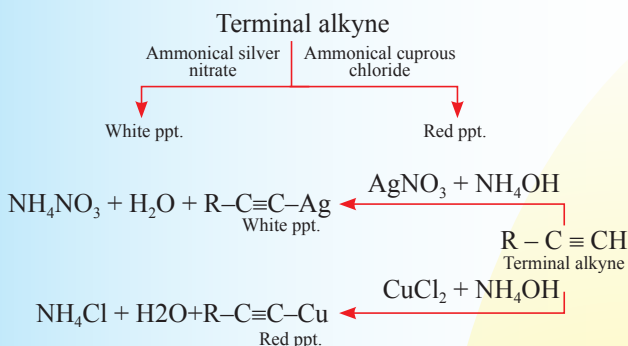
Baeyer's reagent is cold, dilute KMnO₄ solution having pink colour.



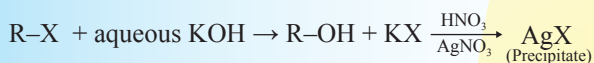
NOTES

The above test are not given by Benzene. Although it has unsaturation.

TEST FOR TERMINAL ALKYNE

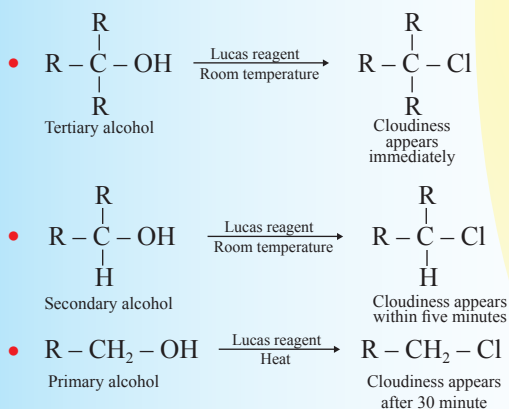


NATURE OF X-GROUP IN C-X BOND

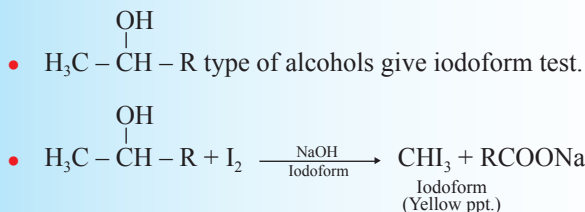


If X is Cl, precipitate will be white and for Br yellow precipitate will be obtained.

DISTINCTION BETWEEN 1°, 2° AND 3° ALCOHOL

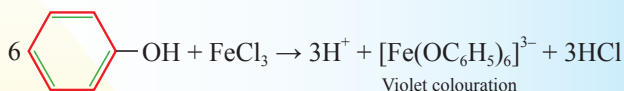


Lucas reagent is anhydrous $\text{ZnCl}_2 + \text{conc. HCl}$.



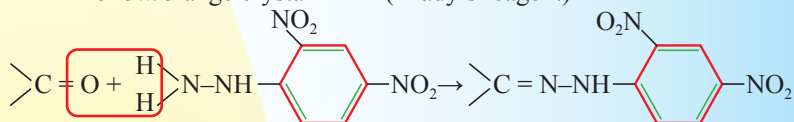
PHENOL

Phenol + ferric chloride \rightarrow Violet colouration
(neutral)

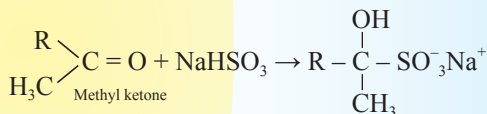
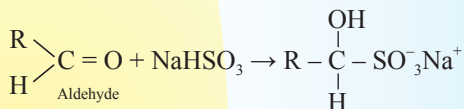


CARBONYL GROUP

- Carbonyl compound + 2, 4-Dinitrophenylhydrazine \rightarrow
Yellow/orange crystal (Brady's reagent)

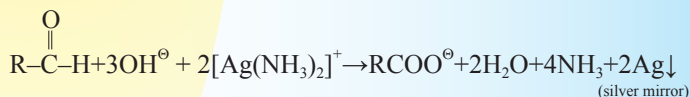


- All aldehydes and only aliphatic methyl ketones
+ $\text{NaHSO}_3 \rightarrow$ White crystalline bisulphite.

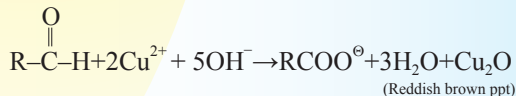


ALDEHYDE GROUP

- Aldehyde + Tollen's reagent \rightarrow Silver mirror



- Aldehyde + Fehling's solution \rightarrow Reddish brown precipitate

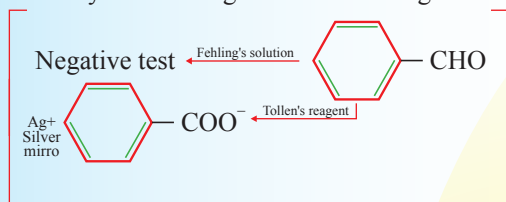


- $\text{H}_3\text{C}-\text{C}(=\text{O})-$ group also give iodoform test



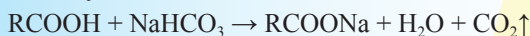
AROMATIC ALDEHYDE GROUP

- Aromatic aldehyde + Tollen's reagent → Silver mirror
- Aromatic aldehyde + Fehling's solution → Negative test

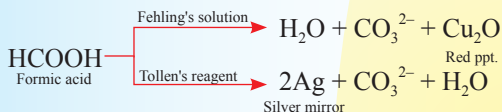


CARBOXYLIC GROUP

Carboxylic acid + Sodium bicarbonate → effervescence



FORMIC ACID



AMINES (1°)



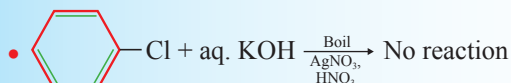
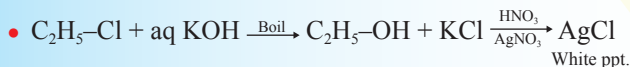
Amines (1°, 2° & 3°) (Hinsberg's test)

- Primary amine + Benzenesulphonyl chloride → Precipitate $\xrightarrow{\text{KOH}}$ Soluble
- Secondary amine + Benzenesulphonyl chloride → Precipitate $\xrightarrow{\text{KOH}}$ insoluble
- Tertiary amine + Benzenesulphonyl chloride → No reaction.

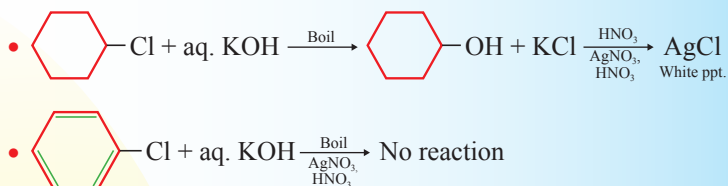


Benzenesulphonyl chloride is called Hinsberg's reagent.

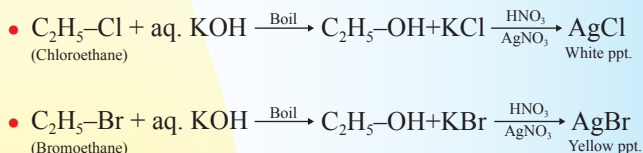
Chloroethane and Chlorobenzene



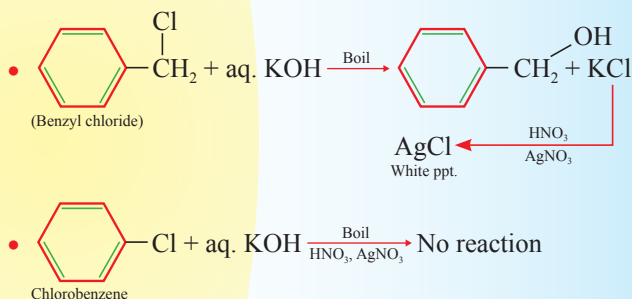
Chlorocyclohexane and chlorobenzene



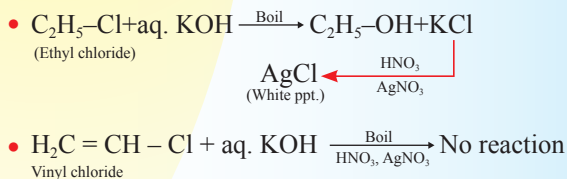
Chlorocyclohexane and bromoethane



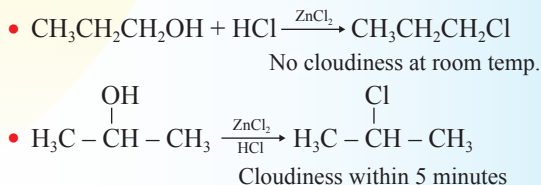
Benzyl chloride and chlorobenzene



Ethyl chloride and vinyl chloride



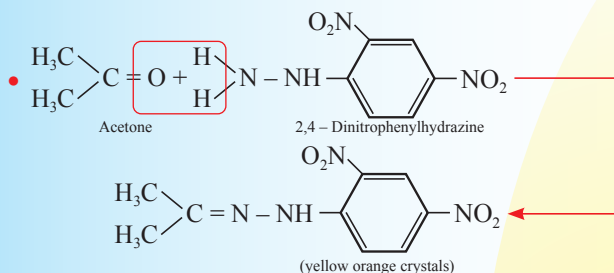
n-Propyl alcohol and iso-propyl alcohol



Ethyl alcohol and methyl alcohol (Iodoform test)

- $\text{CH}_3\text{CH}_2\text{OH} + 4\text{I}_2 + 6\text{NaOH} \rightarrow \text{CHI}_3 + \text{HCOONa}$
Yellow ppt.
- $\text{CH}_3\text{OH} + 4\text{I}_2 + 6\text{NaOH} \rightarrow \text{No yellow ppt.}$

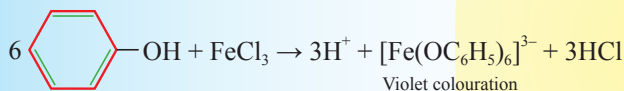
Ethyl alcohol and acetone (2,4 – DNP)



- $\text{C}_2\text{H}_5\text{OH} \xrightarrow{2,4\text{-DNP}}$ No reaction

Phenol and ethyl alcohol (Neutral FeCl_3)

- Phenol + Neutral ferric chloride \rightarrow Violet colouration

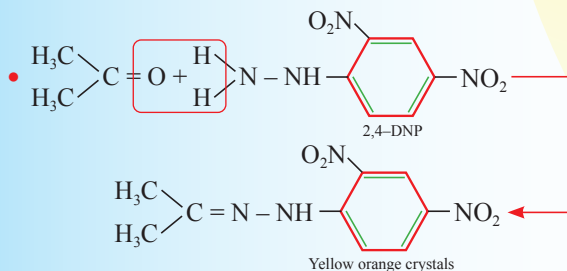


- $\text{CH}_3\text{CH}_2\text{OH} + \text{Neutral ferric chloride} \rightarrow \text{No violet colouration}$

Benzoic acid and phenol (NaHCO_3)

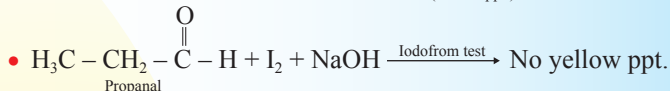
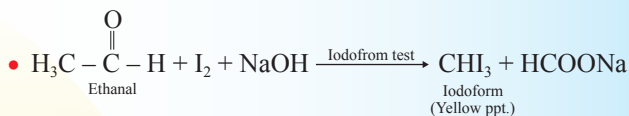
- Benzoic acid + Sodium bicarbonate \rightarrow effervescence
 $\text{C}_6\text{H}_5\text{COOH} + \text{NaHCO}_3 \rightarrow \text{C}_6\text{H}_5\text{COONa} + \text{CO}_2 \uparrow + \text{H}_2\text{O}$
- Phenol + Sodium bicarbonate \rightarrow No effervescence
(Phenol is less acidic than benzoic acid)

Propanone and propanol (2,4 – DNP)



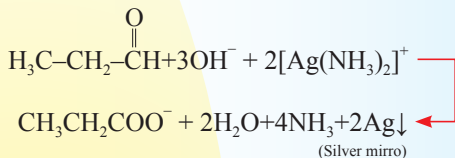
- Propanol + 2,4-Dinitrophenylhydrazine \rightarrow No crystals

Ethanal and propanal (Iodoform test)

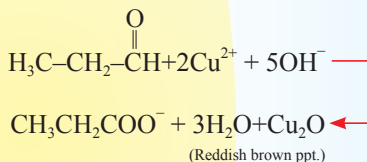


Propanal and propanone (Tollen's and Fehling reagent)

- Propanal + Tollen's reagent → Silver mirror

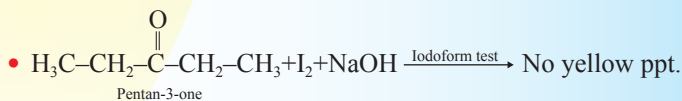
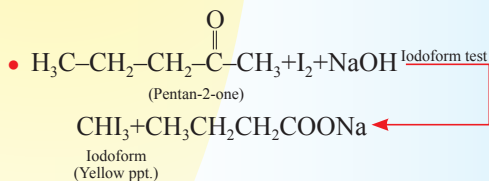


- Propanal + Fehling's solution → Reddish brown precipitate



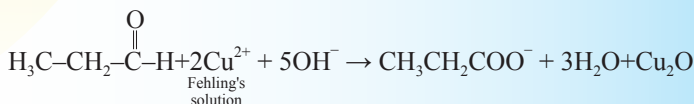
- Propanone $\xrightarrow{\text{Fehling's solution}}$ Negative test
 $\xrightarrow{\text{Tollen's reagent}}$ Negative test

Pentan-2-one and pentan-3-one (Iodoform test)

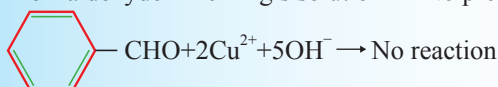


Propanal and benzaldehyde (Fehling solution)

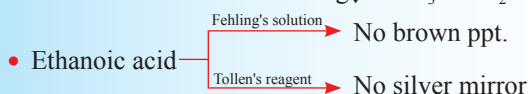
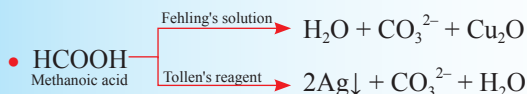
- Propanal + Fehling's solution → Reddish brown precipitate



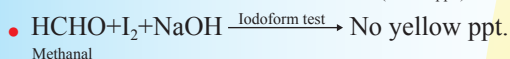
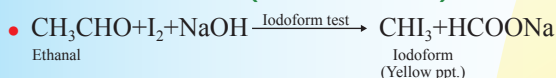
- Benzaldehyde + Fehling's solution → No precipitate



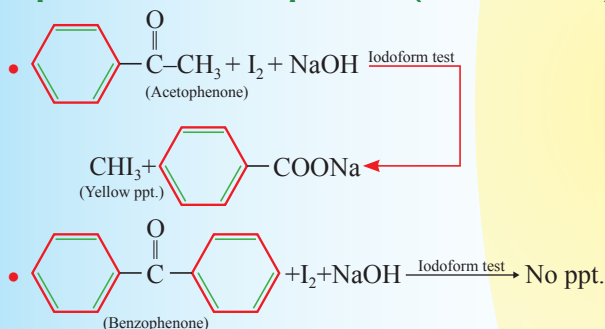
Methanoic acid and ethanoic acid (Tollen's & Fehling solution)



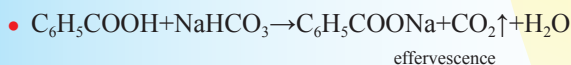
Ethanal and methanal (Iodoform test)



Acetophenone and benzophenone (Iodoform test)



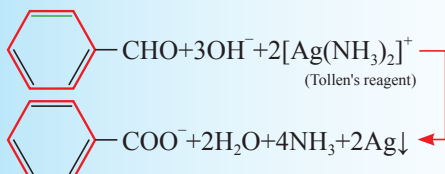
Benzoic acid and ethylbenzoate



- Ethyl benzoate + Sodium bicarbonate → No effervescence

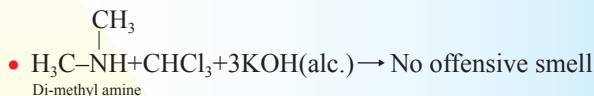
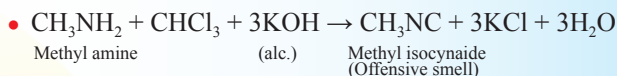
Benzaldehyde and acetophenone (Tollen's test)

- Benzaldehyde + Tollen's reagent → Silver mirror

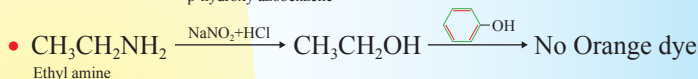
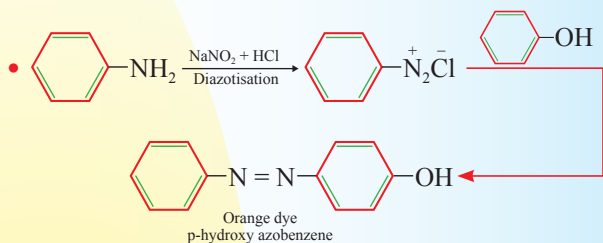


- Acetophenone + Tollen's reagent → No silver mirror

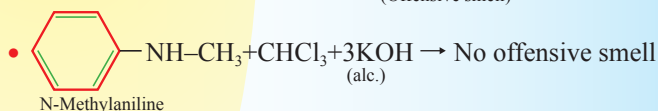
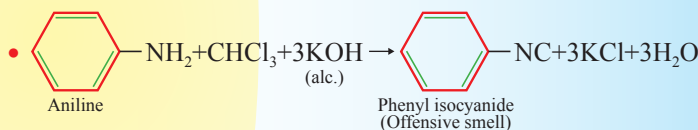
Methyl amine and dimethyl amine (Isocyanide test)



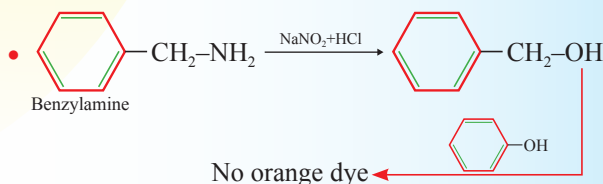
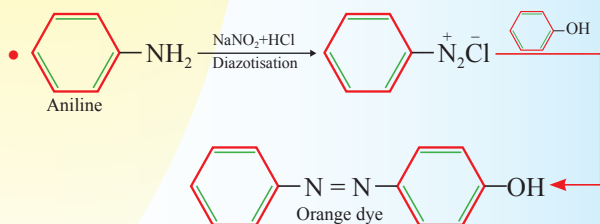
Aniline and ethyl amine (Diazotisation)



Aniline and N-methylaniline (Isocyanide Test)



Aniline and Benzylamine (Diazotisation + phenol)



Glucose and fructose

- $\text{Glucose} + \text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{Gluconic acid} + 2\text{HBr}$
(Brown colour) (Colourless)
- $\text{Fructose} + \text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{Brown colour}$
(Brown colour) (no change in colour)

Glucose and sucrose

- $\text{Glucose} + \text{Tollen's reagent} \rightarrow \text{Silver mirror}$
- $\text{Sucrose} + \text{Tollen's reagent} \rightarrow \text{No silver mirror}$

Glucose and starch

- $\text{Glucose} + \text{Fehling's solution} \rightarrow \text{Red ppt.}$
- $\text{Starch} + \text{Fehling's solution} \rightarrow \text{No red ppt.}$

OR

- $\text{Glucose} + \text{I}_2 \text{ solution} \rightarrow \text{No blue colour}$
- $\text{Starch} + \text{I}_2 \text{ solution} \rightarrow \text{Blue colour}$



Organic Reagents

1. Alcoholic KOH

$R-X \rightarrow$ Alkene; Elimination

2. Aluminium Ethoxide

$R-\overset{\text{O}}{\parallel}{C}-H = O \rightarrow R-\overset{\text{O}}{\parallel}{C}-O-CH_2R$ (Tischenko Reaction)

(Aldehyde) (Ester)

3. Aqueous KOH/NaOH

$R-X \rightarrow ROH$

Nucleophilic substitution reaction also used for Cannizzaro reaction with aldehyde.

4. Baeyer's Reagent (Alkaline cold dilute $KMnO_4$)

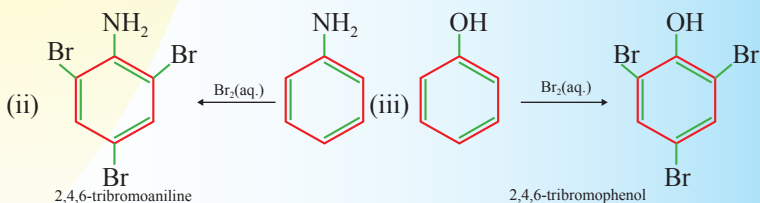
$RCH = CHR' \rightarrow RCH(OH)-CHR'(OH)$
(Syn)

alkene \rightarrow 1, 2 diol

(used to detect unsaturation)

5. Bromine water

(i) Used to detect unsaturation;



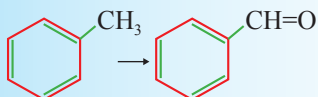
6. Benedict's solution

Used to detect aldehyde group $RCHO \rightarrow RCO_2^-$ [ketone gives -ve test]

7. $\text{Cu}_2\text{Cl}_2 + \text{NH}_4\text{OH}$

Used to Detect Terminal Alkyne
Red Precipitate observed

8. CrO_2Cl_2

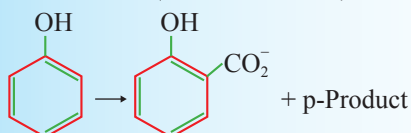


Etard reaction

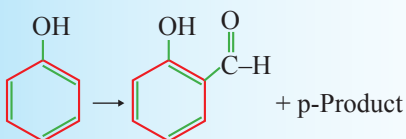
9. CrO_3

- (i) $\text{RCH}_2\text{OH} \rightarrow \text{RCHO}$,
- (ii) $\text{R}_2\text{CHOH} \rightarrow \text{R}_2\text{C=O}$
- (iii) $\text{R}_3\text{COH} \rightarrow$ no reaction

10. $\text{CCl}_4 + \text{OH}^-$ (Reimer Tiemann)

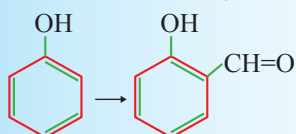


11. $\text{CO} + \text{HCl} + \text{AlCl}_3$



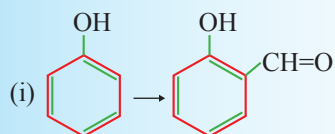
Gatterman Koch reaction

12. $\text{HCN} + \text{HCl} + \text{AlCl}_3$



Gatterman Aldehyde Synthesis

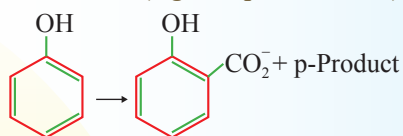
13. $\text{CHCl}_3 + \text{KOH}$



Reimer Tiemann reaction

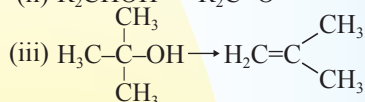
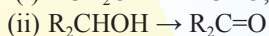
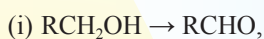
- (ii) $\text{RNH}_2 \rightarrow \text{RNC}$ (*Carbyl amine reaction*)
(used to detect 1° amine) (Isocyanide test)

14. $\text{CO}_2 + \text{OH}^-$ (high temp. + Pressure)



Kolbe's reaction

15. Cu/Δ



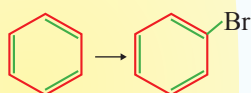
16. 2,4 - D.N.P.

Used to detect carbonyl group (orange ppt. observed)

17. DMSO

Polar aprotic solvent: favour $\text{S}_{\text{N}}2$ mechanism.

18. $\text{Fe} + \text{Br}_2/\text{FeBr}_3$



19. Fehling solution

Used to identify $\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ group.

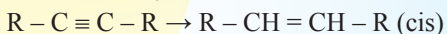
PhCHO gives -ve test

Observation: red ppt. of Cu_2O formed

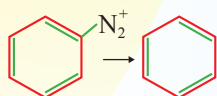
20. Grignard Reagent

Follows (i) Acid base reaction (ii) NAR (iii) NSR

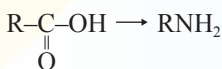
21. $\text{H}_2(\text{Pd}/\text{CaCO}_3)$ Quinoline (Lindlar catalyst)



22. H_3PO_2



23. $\text{HN}_3 + \text{H}_2\text{SO}_4$

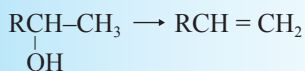


(Schmidt Reaction)

24. $\text{H}_3\text{PO}_4/\Delta$

$\text{H}_3\text{PO}_4 \Rightarrow$ Same as $\text{H}_2\text{SO}_4/\Delta$

25. $\text{H}_2\text{SO}_4/\Delta$



Saytzeff product; C^+ mechanism;

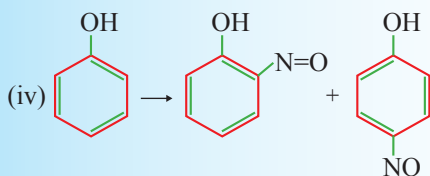
Rearranged alkene can be formed

26. HNO_2 ($\text{NaNO}_2 + \text{HCl}$)

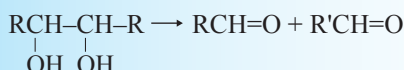
(i) $\text{RNH}_2 \rightarrow \text{R}-\text{OH}$;

(ii) $\text{PhNH}_2 \rightarrow \text{PhN}_2^+$ ($0 - 5^\circ\text{C}$)

(iii) $\text{PhNH}_2 \rightarrow \text{PhOH}$ (high temperature)

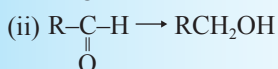
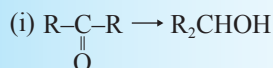


27. HIO_4 (Periodic acid)

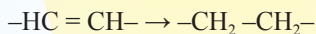


Oxidative cleavage of diol

28. H_2 (Ni) can reduce

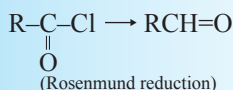


(iii) $\text{RCN} \rightarrow \text{RCH}_2\text{NH}_2$; $-\text{C}\equiv\text{C}- \rightarrow -\text{CH}_2-\text{CH}_2-$,



29. H_2 (Pd/ BaSO_4)

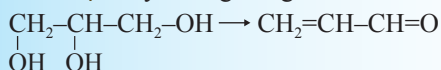
Quinoline

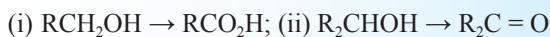
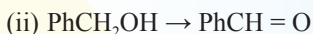
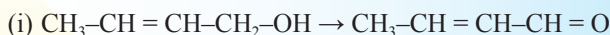


30. Jones Reagent ($\text{CrO}_3 + \text{dil. H}_2\text{SO}_4 + \text{acetone}$)

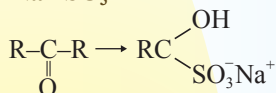
(i) $\text{RCH}_2\text{OH} \rightarrow \text{RCHO}$; (ii) $\text{R}_2\text{CHOH} \rightarrow \text{R}_2\text{C}=\text{O}$

31. KHSO_4 Dehydrating Reagent

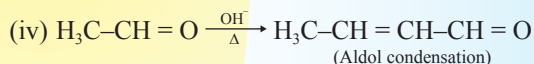
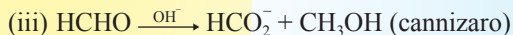
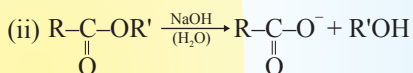
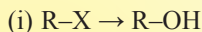


32. $K_2Cr_2O_7/H^+$ **33. MnO_2** 

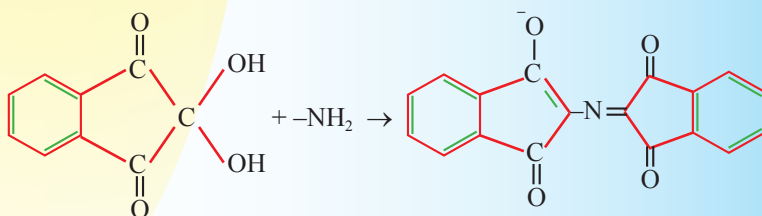
To oxidise allylic/benzylic hydroxyl group into corresponding carbonyl.

34. $NaHCO_3$ **35. $NaHSO_3$** 

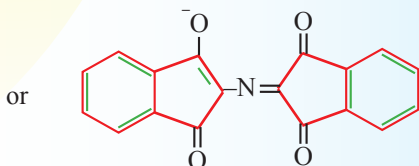
[White crystals, soluble in water used to separate carbonyl from noncarbonyl compound]

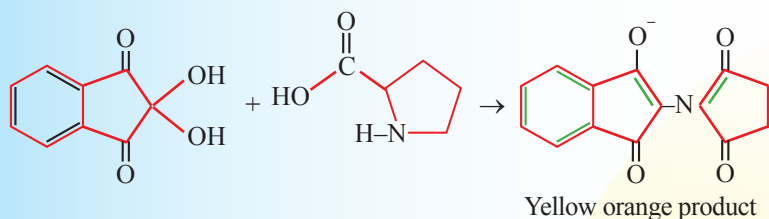
36. $NaOH(aq)$ **37. Ninhydrin**

Detection of amino acid



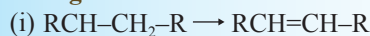
Observation: Purple coloured ion



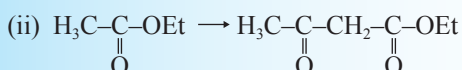


38. NaOR

Strong base:



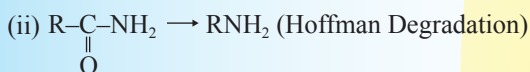
(Saytzeff Product : E₂ elimination)



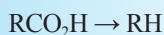
(claisen condensation)

(β keto ester)

39. NaOH + X₂ or NaOX



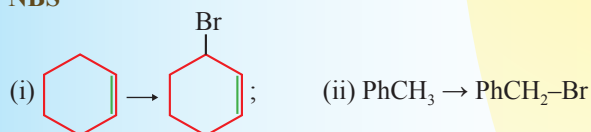
40. NaOH + CaO



41. MnO / 300°C

Used for -CO₂ & -H₂O in carboxylic acid.

42. NBS



43. NaNO₂ + HCl



44. NaNH₂ in paraffin

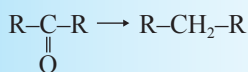
Non-terminal Alkyne → Terminal Alkyne

(2-Butyne → 1-Butyne)

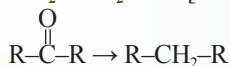
45. Na/EtOH

Reduce all except c/c double & triple bond

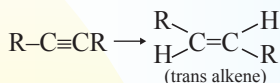
46. Zn(Hg) + HCl [Clemmensen's reduction]



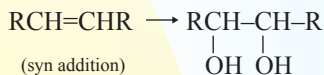
47. $\text{NH}_2-\text{NH}_2/\text{OH}^-$ [Wolf Kishner reduction]



48. Na in Liq. NH_3 [Birch reduction]



49. $\text{OsO}_4 + \text{H}_2\text{O}$

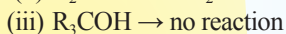


50. O_3 : $\text{R}-\text{CH}=\text{CH}-\text{R} \xrightarrow[\text{H}_2\text{O}/\text{Zn}]{\text{O}_3} \text{R}-\text{CHO} + \text{R}-\text{CHO}$
(Ozonolysis process)

51. Oxirane followed by H^+

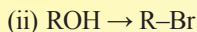
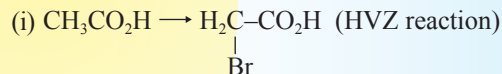


52. PCC

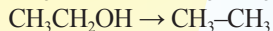
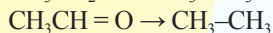
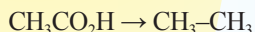


(Mild oxidizing reagent)

53. P(red) + Br_2

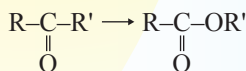


54. P(red) + HI



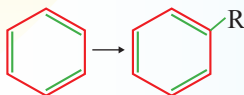
(strong reducing agent can reduce any oxygen or halogen containing compound to alkane)

55. Perbenzoic acid [Baeyer Villiger Oxidation]

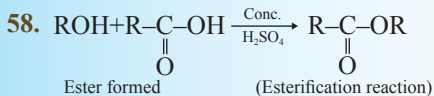
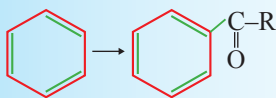


R' having more migrating tendency than R

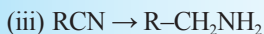
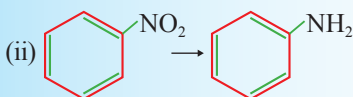
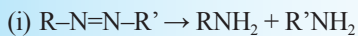
56. $\text{RCI} + \text{AlCl}_3$ [Friedel craft alkylation]



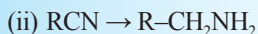
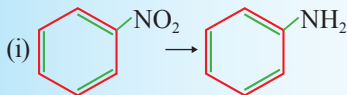
57. $\text{RCOCl} + \text{AlCl}_3$ [Friedel craft acylation]



59. $\text{SnCl}_2 + \text{HCl}$



60. $\text{Sn} + \text{HCl}$



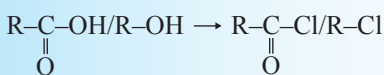
61. Silver salt RCOOAg (Hunsdiecker reaction)



62. $\text{AgOH}/\text{moist Ag}_2\text{O}$; $\text{R}_4\text{N}^+\text{X}^- \rightarrow \text{R}_4\text{NOH}$



63. SOCl_2



64. Tollens Reagent Test

- (i) Terminal alkyne gives
- (ii) Aldehyde Group gives
- (iii) Ketone gives -ve test
- (iv) α -hydroxy ketone gives
- (v) HCOOH gives
- (vi) Hemi acetal gives
- (vii) $\text{PhNH}-\text{OH}$ gives

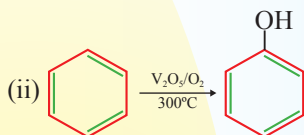
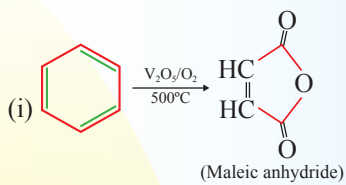
65. Benzene sulphonyl chloride

It is used to distinguish and separate (Hinsberg reagent) 1° , 2° and 3° amines.

66. Tetra ethyl lead (TEL)

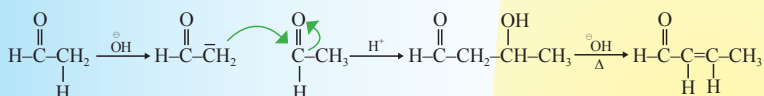
Used as antiknock compound

67. V_2O_5

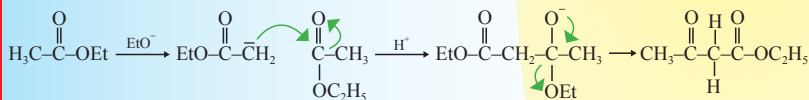


Organic Name Reactions

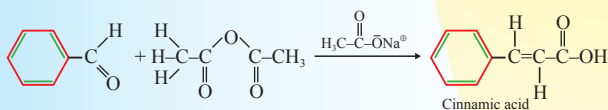
Aldol Condensation



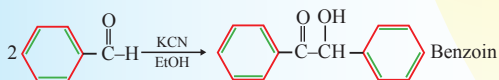
Claisen Condensation



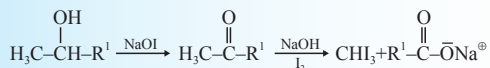
Perkin Condensation



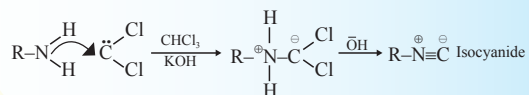
Benzoin Condensation



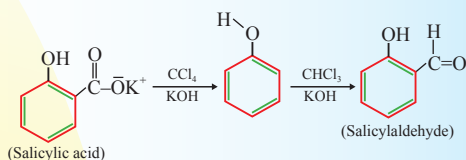
Haloform Reaction



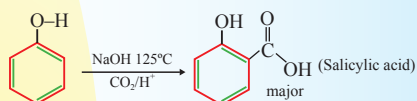
Carbylamine Test



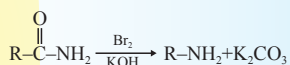
Reimer Tiemann Reaction



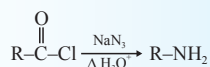
Kolbe's Schimdt Reaction



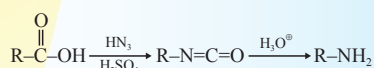
Hoffmann Bromamide Degradation



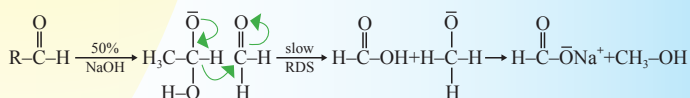
Curtius Reaction



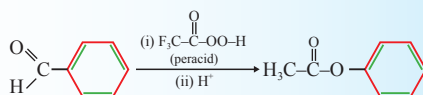
Schmidt Reaction



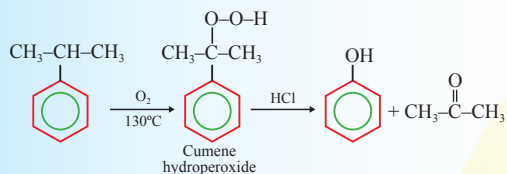
Cannizzaro Reaction



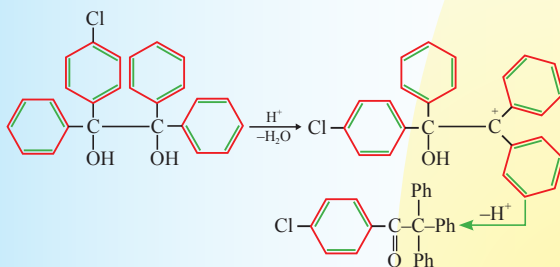
Bayer villiger oxidation



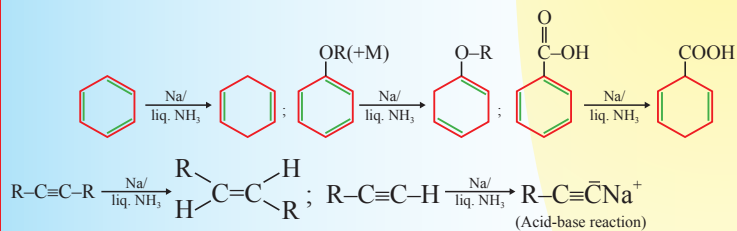
Cumene



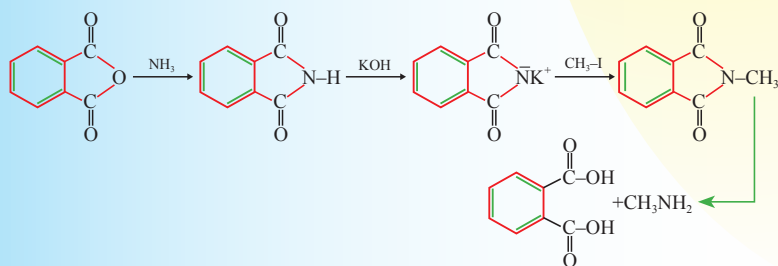
Pinacol-Pinacolone rearrangement

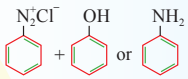

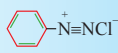




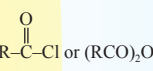


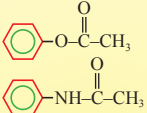
Birch Reduction



Gabriel Synthesis

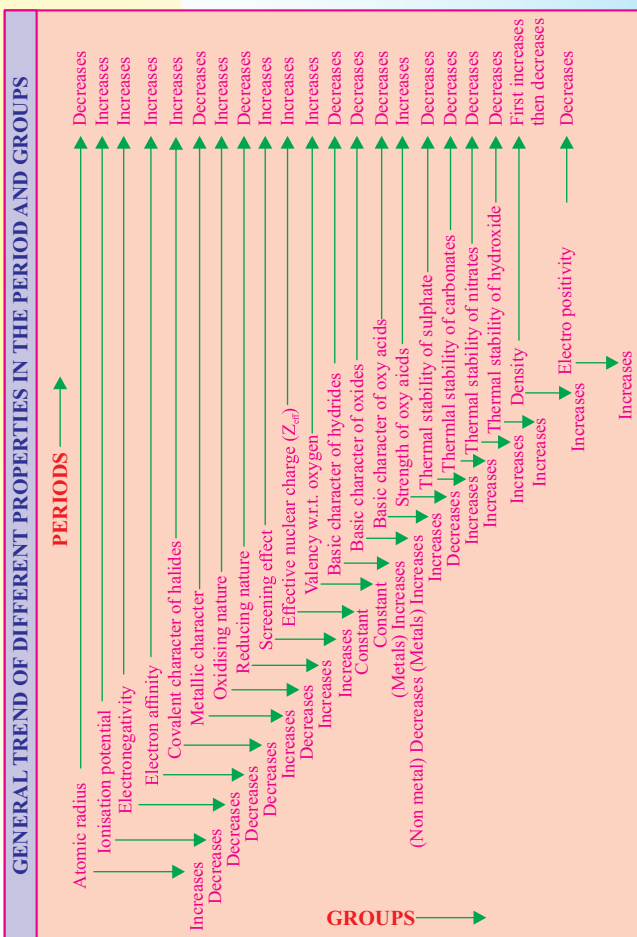


| Name | Reactant | Reagent | Product |
|---------------------------------------|---|--|---|
| Clemmensen Reduction | Aldehyde & Ketone | Zn-Hg/conc. HCl | Alkane |
| Coupling Reaction |  | NaOH (phenol) HCl (Aniline) | Azo Dye (Detection of OH or NH ₂ gr) |
| Diazotization |  | NaNO ₂ + HCl (0° – 5°C) |  |
| Etard reaction |  | CrO ₂ Cl ₂ /CS ₂ |  (Benzaldehyde) |
| Fitting Reaction | Halo benzene | Na/Dry ether | Diphenyl |
| Friedel Craft alkylation |  + R-X | Anhydrous AlCl ₃ | Alkyl Benzene |
| Friedel Craft acylation |  +  or (RCO) ₂ O | Anhydrous AlCl ₃ | Acyl Benzene |
| Gattermann aldehyde synthesis | C ₆ H ₆ | HCN+HCl/ZnCl ₂ / H ₃ O ⁺ | Benzaldehyde |
| Gattermann-Koch reaction | C ₆ H ₆ (CO + HCl) | anhy AlCl ₃ | Benzaldehyde |
| Hell-Volhard-Zelinsky reaction | carboxylic acid having α-hydrogen atom | Br ₂ /red P | α-halogenated carboxylic acid |
| Hoffmann mustard oil reaction | primary aliphatic amine + CS ₂ | HgCl ₂ /Δ | CH ₃ CH ₂ -N=C=S+HgS (black) |
| Hunsdiecker reaction | Ag salt of carboxylic acid | Br ₂ /CCl ₄ , 80°C | alkyl or aryl bromide |
| Kolbe electrolytic reaction | alkali metal salt of carboxylic acid | electrolysis | alkane, alkene and alkyne |
| Mendius reaction | alkyl or aryl cyanide | Na/C ₂ H ₅ OH | primary amine |

| Name | Reactant | Reagent | Product |
|------------------------------------|--------------------------------|---|--|
| Rosenmund reduction | acid chloride | $H_2, Pd/BaSO_4$ boiling xylene | aldehyde |
| Sabatier-Senderens reaction | Unsaturated hydrocarbon | Ranye Ni/ H_2 , 200–300°C | Alkane |
| Sandmeyer reaction | $C_6H_5N_2^+Cl^-$ | CuCl/HCl or CuBr/ HBr or CuCN/KCN, heat | Halo or cyanobenzene |
| Gattermann Reaction | $C_6H_5N_2^+Cl^-$ | Cu/HX(HBr/HCl) | Halobenzene |
| Schotten-Baumann reaction | (phenol or aniline or alcohol) | NaOH + C_6H_5COCl | benzoylated product  |
| Stephen reaction | alkyl cyanide | (i) $SnCl_2/HCl$ (ii) H_2O | Aldehyde |
| Williamson synthesis | alkyl halide | sodium alkoxide or sodium phenoxide | Ether |
| Wurtz-Fitting reaction | alkyl halide + aryl halide | Na/dry ether | alkyl benzene |



Periodic Properties



PERIODICITY

Repetition of properties after regular interval is known as periodicity and these properties are known as periodic properties.

1. Effective Atomic Number
2. Atomic Radius
3. Ionisation Potential
4. Electron Affinity
5. Electro Negativity

ATOMIC RADIUS

Distance between centre of nucleus to outermost electron.

Accurate value of atomic radius cannot be measured therefore operational definitions are used.

- (i) Covalent radius
- (ii) Metallic radius
- (iii) Vander Waal's radius

$$r_{\text{cov}} < r_{\text{metallic}} < r_{\text{vw}}$$

Vander wall radius mainly used for noble gases.

Factors Affecting atomic radius:

(1) $AR \propto \text{Number of shells}$

$$(2) AR \propto \frac{1}{Z_{\text{eff}}}$$

Periodic Trends:

- (1) Generally increases on moving down the group.
- (2) Generally decrease when we are moving left to right in the period.

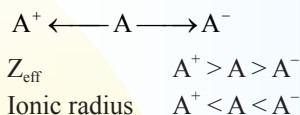


Atomic radius of Al > Ga : Due to poor shielding of 3d subshell electron.
Atomic radius of 4d \approx 5d series element due lanthanide contraction.

Lanthanide Contraction: decrease in atomic/ionic radius with increase in atomic number of lanthanide.

Actinide Contraction: decrease in atomic/ionic radius with increase in atomic number of actinide.

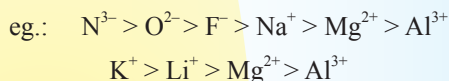
Ionic Radius:



Factors Affecting Ionic Radius

(+) charge \uparrow ionic radius \downarrow
 (-) charge \uparrow ionic radius \uparrow
 $Z_{\text{eff}} \uparrow$ ionic radius \downarrow
 $n \uparrow$ ionic radius \uparrow

\Rightarrow In isoelectronic species (+) charge \uparrow ionic radius \downarrow
 (-) charge \uparrow ionic radius \uparrow

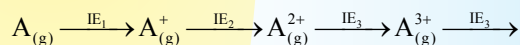


IONIZATION ENERGY

Energy required to remove a loosely bonded e^- from an isolated gaseous atom.

Successive I.E.

IE_1, IE_2, \dots combinedly termed as successive I.E.



$$IE_1 < IE_2 < IE_3 \dots$$

Factors Affecting

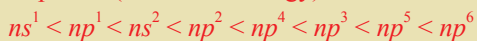
- (1) $IE \propto Z_{\text{eff}}$
- (2) $IE \propto \frac{1}{\text{size}}$
- (2) $IE \propto (+) \text{ charge}$,
- (4) $IE \propto \frac{1}{(-) \text{ charge}}$
- (5) half filled and full filled configuration (affected upto 4th period)
- (6) nature of subshell (affected upto 4th period)

Periodic Trend (s & p-Block)

- (1) Generally decrease on moving down the group
- (2) Generally increase when we are moving left to right in the period.

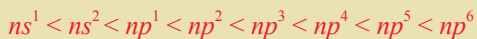
NOTES

upto 4th period (Ionization Energy)



NOTES

after 4th period (Ionization Energy)

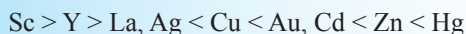


Al < Ga (Poor shielding of 3d subshell e⁻)

Tl > In
Pb > Sn } due to lanthanide contraction

Periodic Trend (d-block)

- (1) Generally increases on moving down the group
- (2) Generally increase when moving left to right in the period.



Application of Ionization Energy

IE↑ Metallic Character ↓

IE↑ Electropositive Character ↓

IE↑ Reducing Property ↓

NOTES

Number of valence e⁻ = highest jump in successive IE

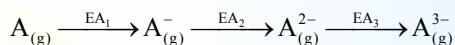
eg.: IE₁ < IE₂ < IE₃ <<< IE₄ < IE₅

Highest jump between IE₃ & IE₄ therefore Ve⁻ is 3

Electron Affinity & Electron Gain Enthalpy

| Electron affinity | Electron gain enthalpy |
|--|-------------------------------------|
| $A_{(g)} \xrightarrow{+e^-} A_{(g)}^-$ | $A_{(g)} + e^- \longrightarrow A^-$ |
| amount of energy | Change in enthalpy |
| released when an e ⁻ | when an e ⁻ is added to |
| is added to isolated | isolated gaseous atom. |
| gaseous atom. | $\Delta H_{eg} = H_p - H_R$ |

Successive Electron Affinity



EA_1 is generally exothermic except N, Be, Mg and Noble gas
 EA_2, EA_3, \dots always endothermic

Factors Affecting

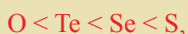
- (1) $EA \propto Z_{\text{eff}}$
- (2) $EA \propto \frac{1}{\text{size}}$
- (3) Nature of subshell
- (4) half and full filled

Periodic Trend

- (1) Generally decreases on moving down the group
- (2) Generally increase when moving left to right in the period.



III^{rd} period element having greater EA than II^{nd} period element except alkali metal.



$|IE_A| = |EA_A|$ and $|EA_A| = |IE_A|$

Electronegativity

Tendency to attract shared pair of e^- towards itself in covalent bond.

Factors Affecting

- (1) $EN \propto Z_{\text{eff}}$
- (2) $EN \propto \frac{1}{\text{size}}$
- (3) $EN \propto \frac{1}{(-)\text{charge}}$
- (4) $EN \propto (+)\text{charge}$,
- (5) $EN \propto \% \text{ s-character of hybrid orbital}$

Periodic Trend

- (1) Generally decreases on moving down the group
- (2) Generally increase when moving left to right in the period.

Application of Electronegative

(1) Polarity of bond

$\Delta EN = 0$ non-polar bond

$\Delta EN \neq 0$ polar bond

(2) Bond parameter

$\Delta EN \uparrow$ Ionic character \uparrow

$\Delta EN \uparrow$ bond length \downarrow

$\Delta EN \uparrow$ bond strength \uparrow

(3) Nature of oxide & oxyacid

E.N. of central atom increase acidic character of oxide and oxyacid increases.

SOME IMPORTANT INCREASING ORDER

1. Abundance of Elements

- (i) Elements on earth crust - Fe, Al, Si, O
- (ii) Metals on earth crust - Ca, Fe, Al
- (iii) Non-metals - Si, O
- In atmosphere - O, N
- In universe - He, Si, H

2. Atomic / Ionic Size

- (i) Mg^{2+} , Na^+ , F^- , O^{2-} , N^{3-}
(Hint: Isoelectronic series)
- (ii) Ca^{2+} , Ar, Cl^- , S^{2-}
- (iii) O, C, S, Se
- (iv) B, Be, Li, Na
- (v) F, O, F^- , O^{2-}

3. Ionization Energy

- (i) Na, Al, Mg, Si
- (ii) Li, B, Be, C, O, N, F, Ne, He (Ist I.P.)
- (iii) Be, C, B, N, F, O, Ne, He, Li (IInd I.P.)

4. Electron Affinity

- (i) I, Br, F, Cl
- (ii) Cu, Ag, Au (EA, of Au is very high = 222 kJ mol⁻¹)
- (iii) O, S, F, Cl
- (iv) N, P, O, S

5. Electronegativity

- (i) As, P, S, Cl (ii) I, Br, Cl, F
(iii) C, N, O, F

6. Hydration of Ions/Hydration Energy

- (i) Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Be^{2+}
(ii) Cs^+ , Rb^+ , K^+ , Na^+ , Li^+
(iii) Na^+ , Mg^{2+} , Al^{3+}

7. Tonic Radii in water

- (i) Cs^+ , Rb^+ , K^+ , Na^+ , Li^+ (ii) Li^+ , Be^{2+}
(iii) Na^+ , Mg^{2+} , Al^{3+}

8. Molar Conductivity in Water

- Li^+ , Na^+ , K^+ , Rb^+ , Cs^+

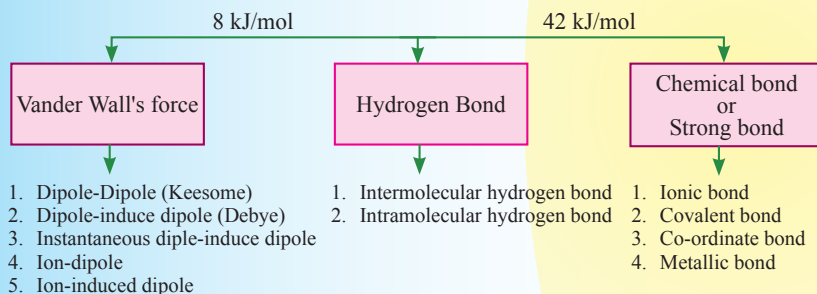


Chemical Bonding

CHEMICAL BOND

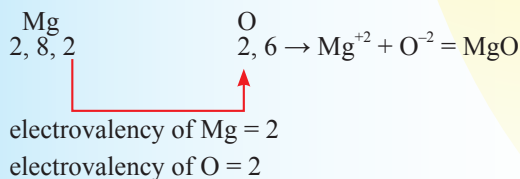
The force of attraction which hold together atom, molecule or ions with in chemical species.

It is always exothermic process.



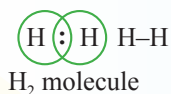
ELECTROVALENT OR IONIC BOND

The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called as Ionic or electrovalent bond.



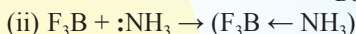
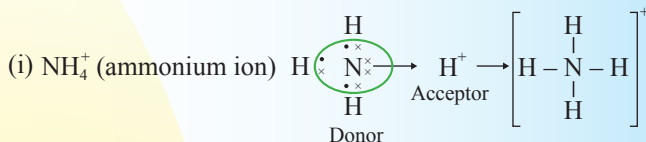
COVALENT BOND

A covalent bond is formed by the mutual sharing of electrons between two atoms to complete their octet. (Except H which completes its duplet)



COORDINATE BOND (DATIVE BOND)

The bond formed between two atom in which contribution of an electron pair is made by one of them while the sharing is done by both.



EXCEPTION OF OCTET RULE

(a) electron deficient

Central atom:

No. of electron < 8

BeH_2

$\text{BF}_3, \text{BCl}_3, \text{BBr}_3, \text{BI}_3$

$\text{AlCl}_3, \text{AlBr}_3, \text{AlI}_3$

(b) electron rich

Central atom:

No. of electron > 8

$\text{PCl}_5, \text{IF}_7$

$\text{SF}_6, \text{XeF}_2$

(c) odd electron species

central atom : has odd

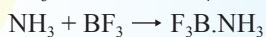
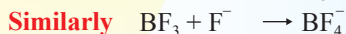
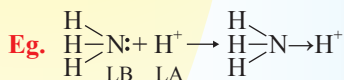
electron $\text{NO}, \text{NO}_2,$

$\text{ClO}_2, \text{ClO}_3$

CO-ORDINATE BOND (DATIVE BOND)

In this type of bond, shared pair of electron donates by one species but shared by both.

- For this type of sharing.
- One species - must have lone pair - act as donar known as Lewis base - acquire +ve charge.
- Another species - must have orbital act as acceptor known as Lewis acid - acquire -ve charge.



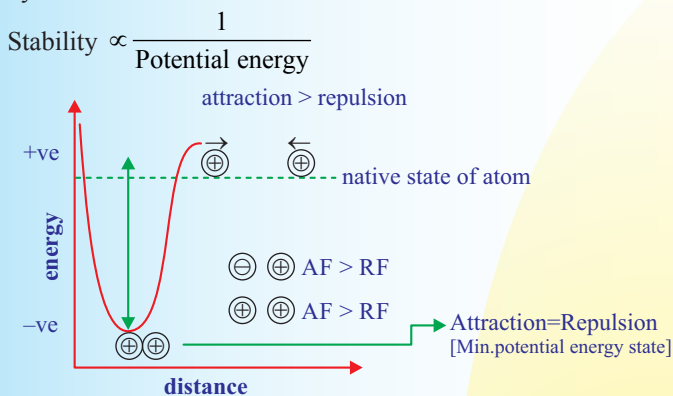
- Donor atom follow octet rule.

MODERN APPROACH OF COVALENT BOND

Consider wave mechanical model of atom means electron has dual nature; wave nature as well as particle nature considered by these theories, there are two theories in this approach.

1. Valence Bond Theory

Proposed by Heitler & London as per VBT bonding takes place for attaining stability.



- Bond formation is an exothermic process.
- During this process some extent of electron cloud merge into each other; this part is known as overlapped region & this process is known as overlapping.

Atom $\left\{ \begin{array}{l} \text{Nucleus} \\ \text{Shell - subshell - orbital - electron - cloud} \end{array} \right.$

2. Molecular Orbital Theory

- Only those orbitals of valence shell can exhibit overlapping which has Unpaired electron

For example H—Cl bond form by overlapping of 1s - 3p orbitals.
 H $\rightarrow 1s^1$
 Cl $\rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5$

- Opposite spin
- **Strength of Covalent Bond**
 Strength of covalent bond \propto extent of overlapping.

1. Nature of Orbitals

(a) **No. of shell:** lower the number of shell higher overlapping.

Bond Strength $\propto \frac{1}{\text{No. of shell}}$ / size of orbitals

$$1-1 > 1-2 > 2-2 > 2-3$$

- **Exception:** $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$ due to
 $\text{O—O} < \text{S—S}$ lp-lp
 $\text{N—N} < \text{P—P}$ repulsion

(b) Type of Sub-shell

Valence shell contain subshell s & p

s-non-directional
p-directional

Directional orbital has
higher extent of overlapping

Possible Combination & Strength of Overlapping

$$s-s < s-p < p-p$$

This factor is applicable when number of shell is same otherwise shell factor prominent.

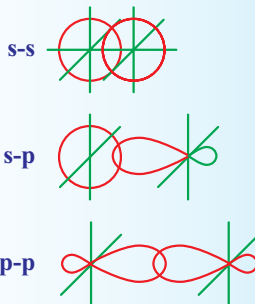
$2s - 2s < 2s - 2p < 2p - 2p$ sub-shell factor

$1s - 1s > 1s - 2s > 1s - 3s$ shell factor

2. Pattern of Overlapping

(a) Axial overlapping:

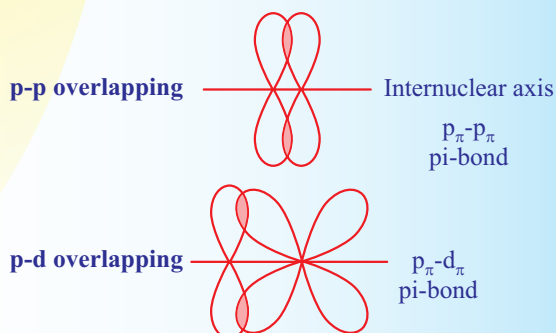
Along the internuclear axis; form sigma (σ) bond, strong bond.



(b) Co-lateral overlapping

Side wise overlapping has less extent of overlapping for π -bond.

Weak bond



HYBRIDISATION

| S.No. | Type or orbital | No. of hybrid orbital | 3D orientation | Example |
|-------|---------------------------|-----------------------------------|------------------------|--------------------------------------|
| 1. | one s + one p | 2; sp | Linear | BeH ₂ , BeCl ₂ |
| 2. | one s + two p | 3; sp ² | Triangular | BCl ₃ , BF ₃ |
| 3. | one s + three p | 4; sp ³ | Tetrahedral | CH ₄ , CCl ₄ |
| 4. | one s + three p + one d | 5; sp ³ d | Triangular bipyramidal | PCl ₅ |
| 5. | one s + three p + two d | 6; sp ³ d ² | Octahedral | SF ₆ |
| 6. | one s + three p + three d | 7; sp ³ d ³ | Pentagonal bipyramidal | IF ₇ |

VALENCE SHELL ELECTRON PAIR REPULSION THEORY

• **Order of repulsion:** lp-lp > lp-bp > bp-bp mb-mb > mb-sb > sb-sb

(mb = multiple bond; sb = single bond)

TYPE OF HYBRIDISATION & POSSIBLE STRUCTURE

| Type of Hybridisation | No. of B.P. | No. of L.P. | Shape | Examples |
|--|-------------|-------------|--|---|
| 1. sp-hybridisation | 2 | - | Linear | BeF ₂ , CO ₂ , CS ₂ , BeCl ₂ |
| 2. (a) sp ² -hybridisation | 3 | - | Trigonal planar | BF ₃ , AlCl ₃ , BeF ₃ ⁻ |
| (b) sp ² -hybridisation | 2 | 1 | V-shape, Angular | NO ₂ , SO ₂ , O ₃ |
| 3. (a) sp ³ -hybridisation | 4 | 0 | Tetrahedral | CH ₄ , CCl ₄ , PCl ₄ ⁺ , ClO ₄ ⁻ , NH ₄ ⁺ , BF ₄ ⁻ , SO ₄ ²⁻ , AlCl ₄ ⁻ , |
| (b) sp ³ -hybridisation | 3 | 1 | Pyramidal | NH ₃ , PF ₃ , ClO ₃ ⁻ , H ₃ O ⁺ , PCl ₃ , XeO ₃ , N(CH ₃) ₃ , CH ₃ ⁻ |
| (c) sp ³ -hybridisation | 2 | 2 | V-shape Angular | H ₂ O, H ₂ S, NH ₂ ⁻ , OF ₂ , Cl ₂ O ₂ , SF ₂ , I ₃ ⁺ |
| 4. (a) sp ³ d-hybridisation | 5 | - | Trigonal bipyramidal | PCl ₅ , SOF ₄ , AsF ₅ |
| (b) sp ³ d-hybridisation | 4 | 1 | See-Saw, folded square distorted tetrahedral | SF ₄ , PF ₄ ⁻ , AsF ₄ ⁻ SbF ₄ ⁻ , XeO ₂ F ₂ |
| (c) sp ³ d-hybridisation | 3 | 2 | almost T-shape | ClF ₃ , ICl ₃ |
| (d) sp ³ d-hybridisation | 2 | 3 | Linear | I ₃ ⁻ , Br ₃ ⁻ , ICl ₂ ⁻ , XeF ₂ |
| 5. (a) sp ³ d ² -hybridisation | 6 | - | Square bipyramidal/ octahedral | PCl ₆ ⁻ , SF ₆ |
| (b) sp ³ d ² -hybridisation | 5 | 1 | Square pyramidal/ distorted octahedral | XeOF ₄ , ClF ₅ , SF ₅ ⁻ , |
| (c) sp ³ d ² -hybridisation | 4 | 2 | Square planar | XeF ₅ ⁺ , XeF ₄ |

| Type of Hybridisation | No. of B.P. | No. of L.P. | Shape | Examples |
|---------------------------------|-------------|-------------|---|-----------|
| 6. (a) sp^3d^3 -hybridisation | 7 | – | Pentagonal bipyramidal | IF_7 |
| (b) sp^3d^3 -hybridisation | 6 | 1 | Pentagonal pyramidal/ distorted octahedral/ capped octahedral | XeF_6 |
| (c) sp^3d^3 -hybridisation | 5 | 2 | Pentagonal planar | XeF_5^- |

DIPOLE MOMENT

Measurement of Polarity in a molecule

$$\boxed{\bar{\mu} = q \times d} \quad \begin{array}{l} \text{debye} = \text{esu}\cdot\text{cm} \\ 1\text{D} = 10^{-18} \text{esu}\cdot\text{cm} \end{array}$$

(A) Identification of polar or Non-polar molecule.

Molecule: Symmetrical distribution of electron cloud-Non-polar.

Molecule: Unsymmetrical distribution of electron cloud-Polar.

Diatomic Molecule

(a) Homoatomic $\Delta EN = 0 \rightarrow \bar{\mu} = 0 \rightarrow$ Non-polar.

H_2, F_2, Cl_2, N_2 etc.

(b) Heteroatomic $\Delta EN \neq 0 \rightarrow \bar{\mu}_{\text{net}} \neq 0 \rightarrow$ polar

$HF > HCl > HBr > HI$

Polyatomic Molecule:

$\mu_R \rightarrow$ vector sum of bond moment

$$\mu_R \rightarrow \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

Important Order

$NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$

$NH_3 > SbH_3 > AsH_3 > PH_3$

$H_2O > H_2S$

$CH_3Cl > CH_3F > CH_3Br > CH_3I$

$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

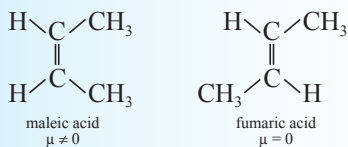
Applications

Predict shape and polarity of molecule

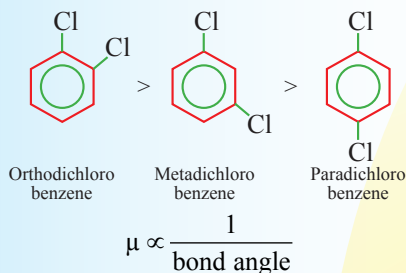
Symmetrical geometry $\rightarrow \mu = 0 \rightarrow$ non-polar

Unsymmetrical geometry $\rightarrow \mu \neq 0 \rightarrow$ polar

Distinguish between cis & trans



Dipole moment in Aromatic Compounds



HYDROGEN BONDING

- It is dipole-dipole type of interaction.
- Electrostatic force of attraction between hydrogen (covalently bond with F/N/O) & highly electronegative atom.
- Hydrogen bond
 - Intermolecular hydrogen bond → between the molecules
 - Intramolecular hydrogen bond → the molecules
- Intromolecular H-bonding takes places mainly in ortho derivatives only.

NOTES

1. Boric acid solid at room temperature (with 2D sheet structure) due to intermolecular hydrogen bonding.
2. In vapour state or in non-polar solvent CH_3COOH as dimer due to intermolecular hydrogen bonding.
3. In vapour phase HF exist as dimer and $(\text{HF})_6$, due to intermolecular hydrogen bonding.
4. Due to intermolecular hydrogen bonding ice has 3D network structure with tetrahedral unit and having open cage structure. The density of ice is less than water.
5. DNA having hydrogen bonds.
6. In hydrated chloral intramolecular hydrogen bond is present.

Strength

Intermolecular H-bond > Intramolecular H-bond

Intramolecular H-bonding takes place in ortho derivatives only.

Applications of H-bonding

| | | |
|-------------------------------|-----------|----------|
| Physical State (dense nature) | \propto | H-bond |
| Melting Point (mp) | \propto | H-bond |
| Boiling Point (bp) | \propto | H-bond |
| Viscosity | \propto | H-bond |
| Surface Tension | \propto | H-bond |
| Volatility | \propto | 1/H-bond |
| Vapour Pressure | \propto | 1/H-bond |

MOLECULAR ORBITAL THEORY (MOT)

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

- Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.
- Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.
- An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule. **Thus an atomic orbital is monocentric while a molecular orbital is polycentric.**
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.
- The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

Formation of Molecular Orbitals:

Linear Combination of Atomic Orbitals (LCAO)

Case I: When two waves are in same phase (constructive interference) the wave adds up and amplitude of new wave is the sum of wave functions of individual atomic orbitals.

$$\psi_{MO} = \psi_A + \psi_B \text{ (Bonding M.O.)}$$

Case II: When two waves are out of phase, the waves are subtracted from each other so that the amplitude of new wave is:

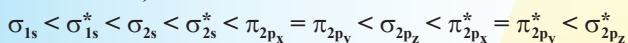
$$\psi_{MO}^* = \psi_A - \psi_B \text{ (Antibonding M.O.)}$$

Condition for Combination Atomic Orbitals

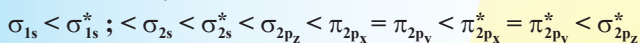
1. The combining atomic orbitals must have the same or nearly the same energy.
2. The combining atomic orbitals must have the same symmetry about the molecular axis.
3. The combining atomic orbitals must overlap to the maximum extent.

Energy level diagram from MOs:

Molecular orbital energy diagram for up to N₂ (molecule having ≤ 14 electrons)



Molecular orbital energy diagram for O₂ and F₂ (molecule having > 14 electrons)



σ^* , π^* = antibonding molecular orbital

σ , π = bonding molecular orbital

Rules of Filling up of Molecular Orbital with Electrons

- (1) The molecular orbital with lower energy will be filled first. (Aufbau Principle)
- (2) The molecular orbital can accommodate maximum only two electrons. (Pauli's exclusion principle)
- (3) If the two MOs have same energy then molecular orbital will first get singly filled and after that pairing will start. (Hunds Rule)

BOND ORDER

Bond order (B.O.) is defined as follows $\text{Bond order (B.O.)} = \frac{1}{2}(N_b - N_a)$

A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative value (i.e., $N_b < N_a$) (i.e., $N_b = N_a$) bond order means an unstable molecule. If bond order zero then molecular does not exist.

NATURE OF THE BOND

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

BOND-LENGTH

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

MAGNETIC NATURE

If one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g.,

1. Boric acid solid at room temperature (with 2D sheet structure) due to intermolecular hydrogen bonding.
2. In vapour state or in non-polar solvent CH_3COOH as dimer due to intermolecular hydrogen bonding.
3. In vapour phase HF exist as dimer and $(\text{HF})_6$, due to intermolecular hydrogen bonding.
4. Due to intermolecular hydrogen bonding ice has 3D network structure with tetrahedral unit and having open cage structure.
The density of ice is less than water.
5. DNA having hydrogen bonds.
6. In hydrated chloral intramolecular hydrogen bond is present. O_2 molecule. Otherwise diamagnetic (e.g.: N_2)

Fractional bond order it will be always paramagnetic

| S.No. | No. of electrons in molecules | N_b | N_a | B.O. | Paramagnetic/ diamagnetic |
|-------|-------------------------------|-------|-------|---------------|---|
| 1. | 1 | 1 | 0 | $\frac{1}{2}$ | paramagnetic |
| 2. | 2 | 2 | 0 | 1 | diamagnetic |
| 3. | 3 | 2 | 1 | 0.5 | paramagnetic |
| 4. | 4 | 2 | 2 | 0 | does not exist |
| 5. | 5 | 3 | 2 | $\frac{1}{2}$ | paramagnetic |
| 6. | 6 | 4 | 2 | 1 | diamagnetic |
| 7. | 7 | 4 | 3 | $\frac{1}{2}$ | paramagnetic |
| 8. | 8 | 4 | 4 | 0 | does not exist |
| 9. | 9 | 5 | 4 | $\frac{1}{2}$ | paramagnetic |
| 10. | 10 | 6 | 4 | 1 | paramagnetic |
| 11. | 11 | 7 | 4 | 1.5 | paramagnetic |
| 12. | 12 | 8 | 4 | 2 | both bond are π C_2 molecule |
| 13. | 13 | 9 | 4 | 2.5 | paramagnetic |
| 14. | 14 | 10 | 4 | 3 | diamagnetic |
| 15. | 15 | 10 | 5 | 2.5 | paramagnetic |
| 16. | 16 | 10 | 6 | 2 | paramagnetic |
| 17. | 17 | 10 | 7 | 1.5 | paramagnetic |
| 18. | 18 | 10 | 8 | 1 | diamagnetic |
| 19. | 19 | 10 | 9 | 0.5 | paramagnetic |
| 20. | 20 | 10 | 10 | 0 | does not exist |

In case of same bond order, stability depends upon
No. of anti-bonding electrons

$$\text{Stability} \propto \frac{1}{\text{No. of anti-bonding } e^-}$$

BONDING PARAMETER

1. Bond length: Internuclear distance

Factor affecting Bond length

(i) Atomic size: bond length \propto size [No. of shell]

(ii) ΔEN , Bond length $\propto \frac{1}{\Delta EN}$

$$d_{A-B} = r_A + r_B - 0.09 \times \Delta EN \text{ \AA}$$

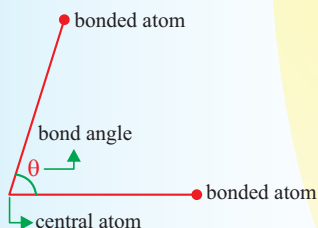
$$\propto \frac{1}{\text{B.O.}}$$

(iii) Bond order: Bond length

(iv) Hybridisation: Bond length $\propto \frac{1}{\% \text{ age of } s\text{-character}}$

Bond Angle

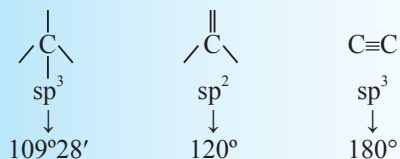
Angle between two adjacent bond is known as bond angle.



FACTORS AFFECTING BOND ANGLE

(i) Hybridisation

Bond angle \propto % age of s-character

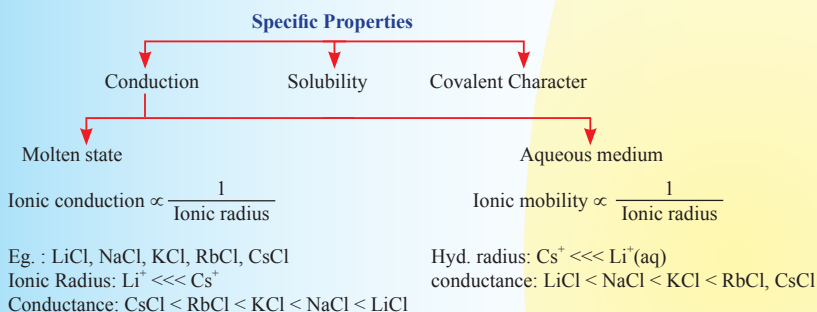


S.E.: should be lower
 I.E.: should be lower
 B.D.E.: should be lower
 ΔH_{eg} : should be higher
 U: should be higher

PROPERTIES OF IONIC SALT

General Properties

Hard, Solid, Brittle (strong electrostatic attraction between ions)
 Non directional nature (ionic compound do not exhibit stereo isomerism)
 Higher Melting Point / Boiling Point
 Isomorphism: $MgSO_4 \cdot 7H_2O$; $ZnSO_4 \cdot 7H_2O$; $FeSO_4 \cdot 7H_2O$



COVALENT CHARACTER / FAJAN'S RULE

Ionic potential of cation (ϕ) $\propto \frac{\text{charge of cation}}{\text{size of cation}}$

Polarisability of anion $\propto \text{size of anion} \propto \text{charge of anion}$

Condition of polarisation

- Smaller cation
- Large anion
- Higher charge

FACTORS AFFECTING POLARISATION

(1) Polarisation \propto charge of cation or anion

- Eg.** (i) $CrO^{+2} < Cr_2O_3^{+3} < CrO_3^{+6}$ Covalent character \uparrow
- (ii) $SF_2^{+2} < SF_4^{+4} < SF_6^{+6}$ Covalent character \uparrow
- (iii) $LiF^{-1} < Li_2O^{-2} < Li_3N^{-3}$ Covalent character \uparrow
 (anion charge \uparrow)

(vi) $\text{NaCl} > \text{CuCl}$

PP \uparrow , CC \uparrow , solubility \downarrow

(vii) $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$

Anionic Size \uparrow , PP \uparrow , CC \uparrow , solubility \downarrow

| HYBRIDISATION OF FOLLOWING SPECIES IN SPECIFIED STATE | | |
|---|--|--|
| Species | Cationic part | Anionic part |
| PCl_5 | PCl_4^+ (sp^3) | PCl_6^- (sp^3d^2) |
| PBr_5 | PBr_4^+ (sp^3) | Br^- |
| XeF_6 | XeF_5^+ (sp^3d^2) | F^- |
| N_2O_5 | NO_2^+ (sp) | NO_3^- (sp^2) |
| I_2Cl_6 (liquid) | ICl_2^+ (sp^3) | ICl_4^- (sp^3d^2) |
| Cl_2O_6 | ClO_2^+ (sp^2) | ClO_4^- (sp^3) |
| I_2 (molten state) | I_3^+ (sp^3) | I_3^- (sp^3d) |

| SILICATES | | | |
|--------------------------|--|---|--------------------------------------|
| Silicates | Sharing of O-atom/Basic Tetrahedral unit | Contribution of O-atom/Basic Tetrahedral unit | General formula |
| Ortho | 0 | 4 | SiO_4^{4-} |
| Pyro | 1 | 3.5 | $\text{Si}_2\text{O}_7^{6-}$ |
| Cyclic | 2 | 3 | $(\text{SiO}_3)_n^{2n-}$ |
| Simple chain (pyroxene) | 2 | 3 | $(\text{SiO}_3)_n^{2n-}$ |
| Double chain (Amphibole) | (3,2) avg. = 2.5 | $\frac{11}{4} = \left(\frac{5.5}{2}\right)$ | $(\text{Si}_4\text{O}_{11})_n^{6n-}$ |
| 2D or (Sheet) | 3 | 2.5 | $(\text{Si}_2\text{O}_5)_n^{2n-}$ |
| 3D | 4 | 2 | $(\text{SiO}_2)_n$ |

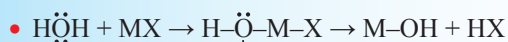
HYDROLYSIS

Hydro - Water

lysis - break down

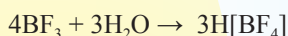
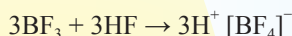
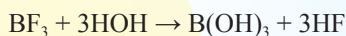
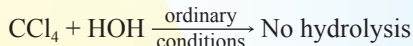
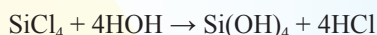
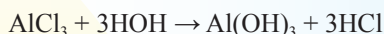
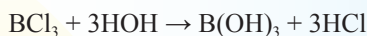
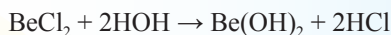
Break down of a molecule through water and formation of new product is known as hydrolysis.

- It is nucleophilic substitution reaction.



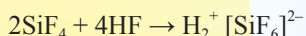
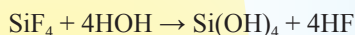
molecule
Intermediate
Product

Extent of Hydrolysis \propto Covalent Character



(partially hydrolysis)

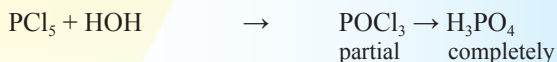
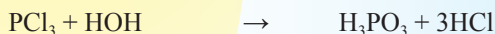
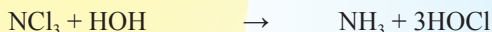
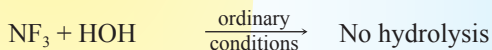
Similarly



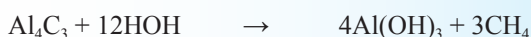
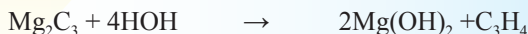
hydrolysis followed by

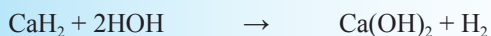
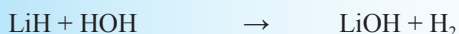
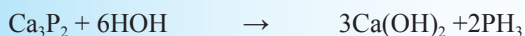
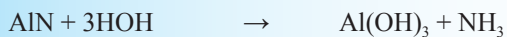
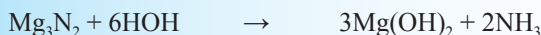
Lewis acid-base reaction.

15th Group Halides

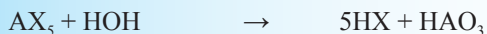
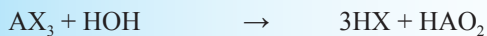


Hydrolysis of Higher Covalent Character Containing Salt





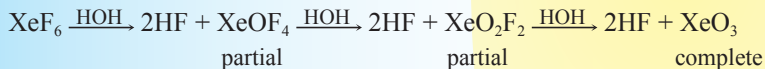
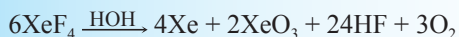
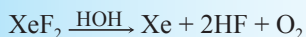
Hydrolysis of Interhalogen Compounds



HX Hydrohalic acid

HOA, HAO₂, HAO₃, HAO₄
oxyacid of halogen

Some Specific Hydrolysis



Back Bonding

It is type of π -interaction between lone pair & vacant orbital of adjacent atom in molecule.

Condition:

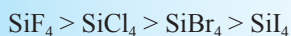
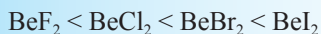
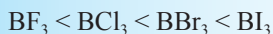
- (i) One atoms must have lone pair.
- (ii) And another atoms must have vacant orbital.

Type of Back Bond:

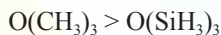
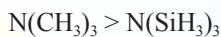
- (i) ($p\pi - p\pi$) type of back bond, eg. BF_3 , BCl_3 , CF_2 , CCl_2
- (ii) ($p\pi - d\pi$) type of back bond
eg. CCl_3^- , $\text{O}(\text{SiH}_3)$, $\text{N}(\text{SiH}_3)_2$, SiH_5O^- , etc.

Application of Back Bonding

Lewis acid character:



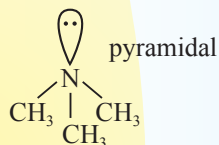
Lewis basic character:



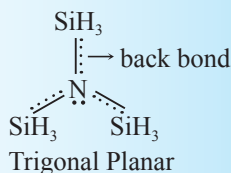
Due to back bonding $\text{B}_3\text{N}_3\text{H}_6$, $(\text{BO}_2)_3^{3-}$, $\text{N}(\text{SiH}_3)_3$ is planar around under lined atom.

Few more examples of Back Bonding

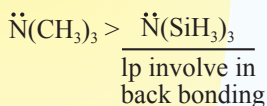
1. Shape of trimethyl amine pyramidal while shape of trisilyl amine is triangular planar.



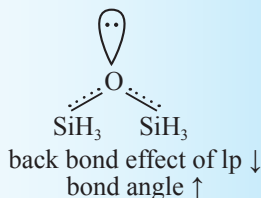
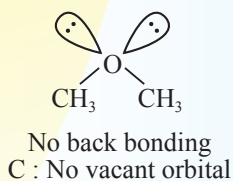
No back bonding due to no vacant orbital in carbon.



2. Lewis base strength



3. Bond angle of $(\text{CH}_3)_2\text{O}$ is very less than $(\text{SiH}_3)_2\text{O}$



Chemical Species having Multicentered Bond

- (3c-2e) bond is also termed as banana bond.
- Bridge bond is stronger than terminal bond.
- Bridge bond is longer than terminal bond.

| | Bridge bond | Hybridisation of central atom |
|---|-------------|--------------------------------|
| Be ₂ Cl ₄ | (3c-4e) | sp ² |
| (BeCl ₂) _n | (3c-4e) | sp ³ |
| Al ₂ Cl ₆ | (3c-4e) | sp ³ |
| I ₂ Cl ₆ | (3c-4e) | sp ³ d ² |
| B ₂ H ₆ | (3c-2e) | sp ³ |
| Be ₂ H ₄ | (3c-2e) | sp ² |
| (BeH ₂) _n | (3c-2e) | sp ³ |
| (AlH ₃) _n | (3c-2e) | sp ³ d ² |
| Al ₂ (CH ₃) ₆ | (3c-2e) | sp ³ |

Odd e⁻ species: Total number of electron or valence electron in odd number.

| | Hybridisation | Shape | Magnetic behaviour |
|--|-----------------|-----------------|--------------------|
| NO ₂ | sp ² | V shape | Para |
| ClO ₂ | sp ² | V shape | Para |
| ClO ₃ | sp ³ | Pyramidal | Para |
| •CH ₃ | sp ² | Trigonal planar | Para |
| •CH ₃ /•CHF ₂ /CH ₂ F | sp ³ | Pyramidal | Para |

OXY-ACIDS

- Mainly oxy-acids are hydroxide of Non-metal oxides.
 - No. of H⁺ ion furnish by an oxy-acid is known as their basicity.
Oxy-acid obtained by dissolving non-metal oxide in water.
Eg. CO₂ + HOH → H₂CO₃ or OC(OH)₂
Here: CO₂ → Non metal oxide - Anhydride of carbonic acid
OC(OH)₂ → Oxyacid
 - NO₂ → Mixed anhydride
 - it gives → HNO₂ & HNO₃
- | Oxide | Acid |
|---------------------------------|---------------------------------|
| N ₂ O ₃ → | HNO ₂ – Nitrous acid |
| N ₂ O ₅ → | HNO ₃ – Nitric acid |

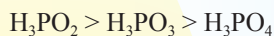
- $P_4O_{10} \rightarrow H_3PO_4$ – Phosphoric acid
- $SO_2 \rightarrow H_2SO_3$ – Sulphurous acid
- $SO_3 \rightarrow H_2SO_4$ – Sulphuric acid
- $Cl_2O_7 \rightarrow HClO_4$ – Perchloric acid

• Oxyacids of different elements

Order of acidic strength



Reducing nature



| Element | Oxide | Oxyacid | Basicity |
|------------|----------|---|---|
| Boron | B_2O_3 | $B(OH)_3$ boric acid | Not protonic acid monobasic Lewis acid |
| Carbon | CO_2 | H_2CO_3 carbonic acid | Two |
| Nitrogen | | $H_2N_2O_2$ Hyponitrous acid HNO_2 Nitrous acid HNO_3 Nitric acid HNO_4 Pernitric acid | |
| Phosphorus | | H_3PO_2 Hypophosphorus acid H_3PO_3 Phosphorus acid H_3PO_4 Ortho phosphoric acid HPO_3 Meta phosphoric acid $H_4P_2O_5$ Pyrophosphorus acid $H_4P_2O_7$ Pyrophosphoric acid $H_4P_2O_6$ Hypophosphoric acid | |

OXYACIDS OF SULPHUR

1. Sulphurous acid - H_2SO_3
2. Sulphuric acid - H_2SO_4
3. Thiosulphuric acid - $H_2S_2O_3$
4. Peroxymonosulphuric (Caro's acid) - H_2SO_5 (Peroxide bond)

5. Peroxydisulphuric acid (Marshal's acid) - $\text{H}_2\text{S}_2\text{O}_8$ (Peroxide bond)
6. Pyrosulphurous acid - $\text{H}_2\text{S}_2\text{O}_5$ - (S-S linkage)
7. Pyrosulphuric acid - $\text{H}_2\text{S}_2\text{O}_7$ (S-O-S linkage)
8. Thionus acid - $\text{H}_2\text{S}_2\text{O}_4$
9. Thionic acid - $\text{H}_2\text{S}_2\text{O}_6$
10. Polythionus acid - $\text{H}_2(\text{S})_n\text{O}_4$ (S-S linkage)
11. Polythionic acid - $\text{H}_2(\text{S})_n\text{O}_6$ (S-S- linkage)

OXYACIDS OF HALOGEN (Cl)

1. Hypochlorous acid - HClO
2. Chlorous acid - HClO_2
3. Chloric acid - HClO_3
4. Perchloric acid - HClO_4

Order of acidic strength: $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$

Oxidising nature: $\text{HClO} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$

ALLOTROPY

- Those substance which are made up of same elements but having different bonding arrangement are known as allotropes & this phenomenon known as allotropy.
- Those elements which exhibit higher tendency of catenation exhibit higher tendency of allotropy.
- Therefore carbon, phosphorus & sulphur exhibit maximum allotropy.

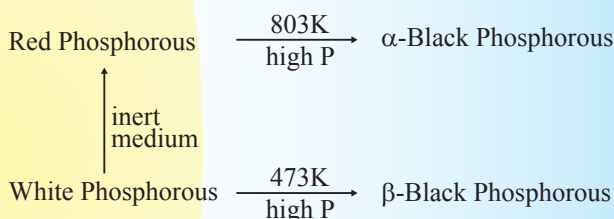
| ALLOTROPE OF CARBON | | |
|---|---|--|
| Diamond | Graphite | Fullerene |
| <p>C-sp^3, tetrahedral structure</p> <p>C-C bond length 1.54\AA</p> <p>Compact 3 dimensional structure</p> <p>Hardest substance</p> <p>Very high mp ($\sim 3400^\circ\text{C}$)</p> <p>Very high density</p> <p>Non conductor</p> <p>Very high refractive index</p> <p>Exhibit total internal reflection</p> <p>Shines bright in light</p> | <p>Hexagonal layer structure</p> <p>All sp^2 hybrid carbon</p> <p>Unhybrid orbital electron form</p> <p>π-bond. This π-bond exhibit resonance and due to resonance there is mobility of electrons and it becomes conductor of electricity.</p> | <p>Latest discovered allotrope of carbon it is found in chimney sooty particle.</p> <p>It contain C_{60}-C_{320}. C : sp^2 hybrid</p> <p>Contain pentagon & hexagonal structure</p> <p>C_{60}: Buckminster fullerene soccer ball (Football) or bucky ball.</p> <p>C_{60}: 20 hexagon rings 12 pentagon rings</p> <p>Purest form of carbon</p> <p>No dangling bond</p> |

ALLOTROPES OF PHOSPHOROUS

(a) White phosphorous (b) Red phosphorous (c) Black phosphorous

| White phosphorous | Red Phosphorous |
|---|---|
| Waxy solid | Brittle powder |
| Poisonous | Non poisonous |
| Soluble in CS ₂ , Insoluble in water | Insoluble in water & CS ₂ |
| Monomer of P ₄ | Polymer of P ₄ |
| Highly reactive due to bond angle strain | More stable than white phosphorous |
| It glows in dark due to slow oxidation (phosphorescence) | It does not glow in dark |
| It gives phosphine (PH ₃) on reaction with NaOH | It gives hypo phosphoric acid on reaction with NaOH |

Order of stability of MP or density → white < red < black



| ALLOTROPES OF SULPHUR | |
|--|---|
| Crystalline | Amorphous |
| Rhombic sulphur (α -S) most stable form Monoclinic sulphur (β -S) $\alpha\text{-S} \xrightleftharpoons[<95.6^\circ\text{C}]{>95.6^\circ\text{C}} \beta\text{-S}$ 95.6°C = transition Temperature both are soluble in CS ₂ but insoluble in water | Milk of sulphur Plastic sulphur (γ -S) Colloidal sulphur $\underset{\text{RA}}{\text{H}_2\text{S}} + \underset{\text{OA}}{2\text{HNO}_3} \xrightarrow{\text{Redox}} \text{S} + 2\text{NO}_2 + 2\text{H}_2\text{O}$ |

- Density of α S > β S.
- Both are puckered crown shape having S₈ units.
- S₂ is paramagnetic sulphur which exist in vapour form at high temperature.
- S₆ is chair form of S.

Effect of Temperature



SOME IMPORTANT INCREASING ORDER

1. Acidic property

- (i) $\text{SiO}_2, \text{CO}_2, \text{N}_2\text{O}_5, \text{SO}_3$
- (ii) $\text{MgO}, \text{Al}_2\text{O}_3, \text{SiO}_2, \text{P}_4\text{O}_{10}$
- (iii) $\text{HClO}, \text{HClO}_2, \text{HClO}_3, \text{HClO}_4$
- (iv) $\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{HF}$
- (v) $\text{SiH}_4, \text{PH}_3, \text{H}_2\text{S}, \text{HCl}$
- (vi) $\text{H}_2\text{O}, \text{H}_2\text{S}, \text{H}_2\text{Se}, \text{H}_2\text{Te}$
- (vii) $\text{HF}, \text{HCl}, \text{HBr}, \text{HI}$
- (viii) $\text{InCl}_3, \text{GaCl}_3, \text{AlCl}_3$
- (ix) $\text{BF}_3, \text{BCl}_3, \text{BBr}_3, \text{BI}_3$

2. Bond Angle

- (i) $\text{CH}_4, \text{C}_2\text{H}_4, \text{C}_2\text{H}_2$
- (ii) $\text{H}_2\text{O}, \text{NH}_3, \text{CH}_4, \text{CO}_2$
- (iii) $\text{H}_2\text{O}, \text{NH}_3, \text{CH}_4, \text{BH}_3$
- (iv) $\text{NO}_2^-, \text{NO}_2, \text{NO}_2^+$
- (v) $\text{H}_2\text{Se}, \text{H}_2\text{S}, \text{H}_2\text{O}$
- (vi) $\text{AsH}_3, \text{PH}_3, \text{NH}_3$
- (vii) $\text{PF}_3, \text{PCl}_3, \text{PBr}_3, \text{PI}_3$
- (viii) $\text{NF}_3, \text{NCl}_3$
- (ix) $\text{NF}_3, \text{NH}_3, \text{NCl}_3$
- (x) $\text{OF}_2, \text{OH}_2, \text{Cl}_2\text{O}$

3. Basic Character

- (i) $\text{LiOH}, \text{NaOH}, \text{KOH}, \text{RbOH}, \text{CsOH}$
- (ii) $\text{Be}(\text{OH})_2, \text{Mg}(\text{OH})_2, \text{Ca}(\text{OH})_2, \text{Ba}(\text{OH})_2$
- (iii) $\text{BeO}, \text{MgO}, \text{CaO}, \text{SrO}$
- (iv) $\text{NiO}, \text{MgO}, \text{SrO}, \text{K}_2\text{O}, \text{Cs}_2\text{O}$
- (v) $\text{CO}_2, \text{B}_2\text{O}_3, \text{BeO}, \text{Li}_2\text{O}$
- (vi) $\text{SiO}_2, \text{Al}_2\text{O}_3, \text{MgO}, \text{Na}_2\text{O}$
- (vii) $\text{SbH}_3, \text{AsH}_3, \text{PH}_3, \text{NH}_3$
- (viii) $\text{F}^-, \text{OH}^-, \text{NH}_2^-, \text{CH}_3^-$

4. Thermal Stability

- (i) $\text{Li}_2\text{CO}_3, \text{Na}_2\text{CO}_3, \text{K}_2\text{CO}_3, \text{Rb}_2\text{CO}_3, \text{Cs}_2\text{CO}_3$
- (ii) $\text{BeCO}_3, \text{MgCO}_3, \text{CaCO}_3, \text{BaCO}_3$

(iii) $\text{Be}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$
Polarisation

(iv) LiOH , NaOH , KOH , RbOH , CsOH

(v) BeSO_4 , MgSO_4 , CaSO_4

(vi) CsH , RbH , KH , NaH , LiH

(vii) SbH_3 , AsH_3 , PH_3 , NH_3

(viii) H_2Te , H_2Se , H_2S , H_2O

(ix) HI , HBr , HCl , HF

5. Ionic Character

(i) LiBr , NaBr , KBr , RbBr , CsBr

(ii) LiF , NaF , KF , RbF , CsF

(iii) BeCl_2 , MgCl_2 , CaCl_2 , SrCl_2 , BaCl_2

(iv) BCl_3 , AlCl_3 , GaCl_3

(v) VCl_4 , VCl_3 , VCl_2

(vi) AlF_3 , Al_2O_3 , AlF_3

(vii) AlN , Al_2O_3 , AlF_3

(viii) HI , HBr , HCl , HF

(ix) CuCN , AgCN

(x) AgCl , KCl

6. Oxidizing Power

(i) $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^-

(ii) MnO_4^{2-} , MnO_4^-

(iii) WO_3 , MoO_3 , CrO_3

(iv) GeCl_4 , SnCl_4 , PbCl_4

(v) I_2 , Br_2 , Cl_2 , F_2

(vi) Zn^{+2} , Fe^{+2} , Pb^{2+} , Cu^{2+} , Ag^+

7. Melting Point

(i) Cs , Rb , K , Na , Li

(ii) Mg , Ba , Sr , Ca , Be

(iii) CaI_2 , CaBr_2 , CaCl_2 , CaF_2

(iv) BeCl_2 , MgCl_2 , CaCl_2 , SrCl_2 , BaCl_2

(v) NaI , NaBr , NaCl , NaF

(vi) CsCl , RbCl , KCl , NaCl

(vii) AlCl_3 , MgCl_2 , NaCl

8. Density

- (i) Na, Al, Fe, Pb, Au
- (ii) Li, K, Na, Rb, Cs
- (iii) Ca, Mg, Be, Sr, Ba
- (iv) Highest Density = Os/Ir
- (v) Lowest density = H
- (vi) Metal of lowest Density = Li

9. Boiling Point

- (i) PH_3 , AsH_3 , NH_3 , SbH_3
- (ii) H_2S , H_2Se , H_2O
- (iii) HCl , HBr , HI , HF
- (iv) NH_3 , HF , H_2O
- (v) He, Ne, Ar, Kr
- (vi) H_2O , D_2O
- (vii) H_2 , Cl_2 , Br_2

10. Electrical Conductivity

Cr, Pt, Fe, Al, Au, Cu, Ag

11. Reactivity with water

- (i) Li, Na, K, Rb, Cs
- (ii) Be, Mg, Ca, Sr, Ba

12. Extent of Hydrolysis

- (i) CCl_4 , MgCl_2 , AlCl_3 , SiCl_4 , PCl_5
- (ii) BiCl_3 , SbCl_3 , AsCl_3 , PCl_3 , NCl_3

13. Bond Strength

- (i) HI , HBr , HCl , HF
- (ii) $\overset{\curvearrowright}{\text{C}}-\text{I}$, $\overset{\curvearrowright}{\text{C}}-\text{Br}$, $\overset{\curvearrowright}{\text{C}}-\text{Cl}$, $\overset{\curvearrowright}{\text{C}}-\text{F}$
- (iii) $\text{N}-\text{N}$, $\text{N}=\text{N}$, $\text{N}\equiv\text{N}$
- (iv) $\text{As}-\text{H}$, $\text{Sb}-\text{H}$, $\text{P}-\text{H}$, $\text{N}-\text{H}$
- (v) N_2^{2-} , N_2^- , N_2^+ , N_2
- (vi) O_2^{2-} , O_2^- , O_2 , O_2^+ , O_2^{2+}
 - LiI, LiBr, LiCl, LiF NaI, NaBr, NaCl, NaF
 - CsCl, RbCl, KCl, NaCl BaO, SrO, CaO, MgO
- (vii) F_2 , H_2 , O_2 , N_2

- (viii) NO^- , NO , NO^+
- (ix) I_2 , F_2 , Br_2 , Cl_2
- (x) $\text{O}-\text{O}$, $\text{S}-\text{S}$
- (xi) $\text{F}-\text{F}$, $\text{O}-\text{O}$, $\text{N}-\text{N}$, $\text{C}-\text{C}$, $\text{H}-\text{H}$

14. Reducing Power

- (i) PbCl_2 , SnCl_2 , GeCl_2
- (ii) HF , HCl , HBr , HI
- (iii) Ag , Cu , Pb , Fe , Zn
- (iv) HNO_3 , H_2SO_3 , H_2S
- (v) H_3PO_4 , H_3PO_3 , H_3PO_2

15. Covalent Character

- (i) LiCl , BeCl_2 , BCl_3 , CCl_4
- (ii) SrCl_2 , CaCl_2 , MgCl_2
- (iii) TiCl_2 , TiCl_3 , TiCl_4
- (iv) LiCl , LiBr , LiI
- (v) Na_2O , Na_2S
- (vi) AlF_3 , Al_2O_3 , AlN
- (vii) HF , HCl , HBr , HI

16. Strength of Hydrogen bonding ($\text{X}\dots\text{H}-\text{X}$)

- (i) S , Cl , N , O , F
- (ii) NH_3 , H_2O , HF

17. Reactivity with Hydrogen

- (i) Cs , Rb , K , Na , Li
- (ii) Ba , Sr , Ca , Mg , Be

18. Reactivity Towards Air

Be , Mg , Cs , Sr , Ba

19. Bond Length

- (i) N_2 , O_2 , F_2 , Cl_2
- (ii) $\text{N}-\text{N}$, $\text{C}-\text{N}$, $\text{C}-\text{C}$
- (iii) CO , $\text{C}=\text{O}$, $-\text{C}-\text{O}-$
- (iv) NO^+ , NO , NO^-
- (v) O_2 , O_3 , H_2O_2 ($\text{O}-\text{O}$ bond length)

- (vi) CO , CO_2 , CO_3^{-2}
- (vii) N_2 , N_2^- , N_2^{-2}
- (viii) O_2^{+2} , O_2 , O_2^- , O_2^{-2}
- (ix) HF , HCl , HBr , HI

20. Dipole moments

- (i) CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl
- (ii) NF_3 , NH_3 , H_2O , HF
- (iii) Cis-chloropropene, Trans-chloropropene
- (iv) p, m, o-dichlorobenzene
- (v) CH_3I , CH_3Br , CH_3F , CH_3Cl
- (vi) NH_3 , SO_2 , H_2O , HF
- (vii) H_2S , H_2O
- (viii) HI , HBr , HCl , HF
- (ix) PH_3 , AsH_3 , SbH_3 , NH_3
- (x) H_2O , H_2O_2

| Group 15 | Bond angle | Group 16 | Bond angle |
|----------------|-----------------|-----------------------|-----------------|
| NH_3 | $107^\circ 48'$ | H_2O | $104^\circ 28'$ |
| PH_3 | $93^\circ 36'$ | H_2S | 92° |
| AsH_3 | $91^\circ 48'$ | H_2Se | 91° |
| SbH_3 | $91^\circ 18'$ | H_2Te | 90.5° |

INERT PAIR EFFECT

Inert pair effect the reluctance of ns electrons to take part in bond formation is called inert pair effect. This effect is more pronounced in heavier elements and that too for 13, 14 and 15 group. It results in the decrease in oxidation state by 2 units. For example, Tl is more stable in oxidation state + 1 than the oxidation state +3.

In p-block elements the stability of the lower oxidation state increases on descending the group.

Group 13

- B (+3)
- Al (+3)
- Ga (+3), (+1)
- In (+3), (+1)
- Tl (+3), (+1)

Group 14

- C (+4)
- Si (+4)
- Ge (+4), (+2)
- Sn (+4), (+2)
- Pb (+4), (+2)

Order of stability

$Tl^{+1} > In^{+1} > Ga^{+1}$ (due to inert pair effect)

Order of stability

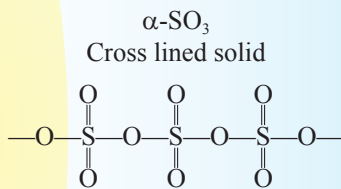
$Pb^{+2} > Sn^{+2} > Ge^{+2}$ (due to inert pair effect)

Molecules that do not Exist

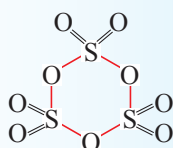
- (1) SF_4 , SF_6 & PF_5 exist while OF_4 , OF_6 , NF_5 do not exist.
- (2) (a) PI_5 (vap) & SCl_6 do not exist.
(b) SCl_6 does not exist while $TeCl_6$ exist.
(c) PI_5 (Solid) exist
- (3) SF_6 , PF_5 , XeF_6 , XeF_4 & XeF_2 exist while SH_6 , PH_5 , XeH_6 , XeH_4 , XeH_2 do not exist.

ALLOTROPIC FORM OF SO_3

SO_3 have three allotropic form α - SO_3 , β - SO_3 and γ - SO_3 .



Polymeric chain structure
 β - SO_3



γ - SO_3
(S_3O_9)
cyclic trimer



s-Block Elements

ALKALI METALS

Physical Properties

General electronic configuration ns^1 .

General oxidation state + 1

Atomic/Ionic size $Li < Na < K < Rb < Cs$.

Density $Li < K < Na < Rb < Cs$

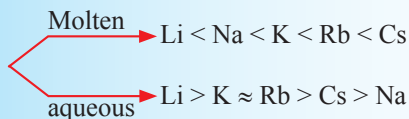
Ionisation energy $Li > Na > K > Rb > Cs$

Flame colour

| | |
|----|----------------|
| Li | Crimsen red |
| Na | Golden yellow |
| K | Pale violet |
| Rb | Reddish violet |
| Cs | Blue |

Basic nature increase down to the group

Reducing Property

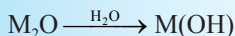


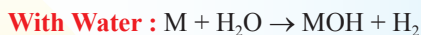
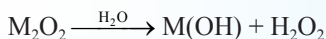
Chemical Properties

With O_2 : Lithium forms normal oxide $[Li_2O]$

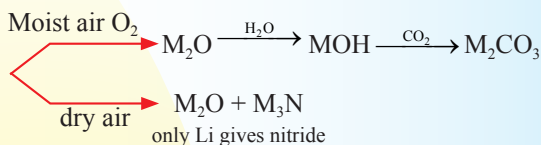
Sodium forms peroxide (Na_2O_2)

K, Rb, Cs forms superoxide KO_2, RbO_2, CsO_2

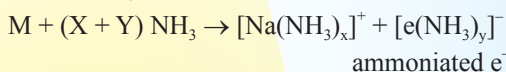




With Air

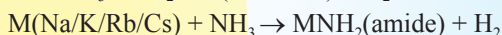
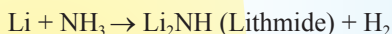


With NH₃

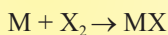


Paramagnetic, blue colour. In excess of metal dimagnetic and copper bronze colour.

on standing



With Halides



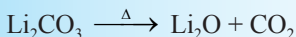
K, Rb, Cs forms poly halide due to large size

SIMILARITIES BETWEEN LITHIUM AND MAGNESIUM

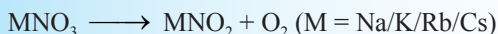
- Both lithium and magnesium are harder and lighter than other elements in the respective groups.
- Lithium and magnesium react slowly with cold water.
Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride by direct combination with nitrogen, Li₃N and Mg₃N₂.
- The oxides, Li₂O and MgO do not combine with excess oxygen to give a peroxide or a superoxide.
- The carbonates of lithium and magnesium decompose easily on heating to form the oxide and CO₂. Solid bicarbonates are not formed by lithium and magnesium.
- Both LiCl and MgCl₂ are soluble in ethanol.
- Both LiCl and MgCl₂ are deliquescent and crystallise from aqueous solution as hydrates,
LiCl.2H₂O and MgCl₂.8H₂O.

Carbonates

Only Li_2CO_3 decomposes

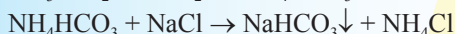


Nitrates



$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (Washing Soda)

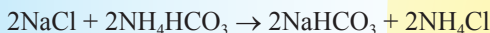
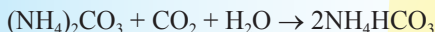
- In **Solvay's process**, CO_2 gas is passed through saturated brine (NaCl) solution when sparingly soluble NaHCO_3 separates out.



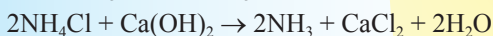
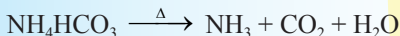
The NaHCO_3 formed above is calcined to form Na_2CO_3



- The reactions taking place at different stages during the manufacture of Na_2CO_3 by Solvay process are given as under :



- (b) Ammonia recovery tower



- (c) Calcination of NaHCO_3



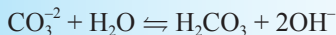
- (i) **Efflorescence** : $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ when exposed to air it gives out nine out of ten H_2O molecules.



(Monohydrate)

This process is called efflorescence. Hence washing soda losses weight on exposure to air.

- (ii) **Hydrolysis**: Aqueous solution of Na_2CO_3 is alkaline in nature due to anionic hydrolysis.

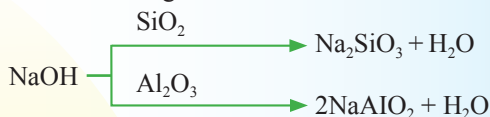


(Carbonic acid)

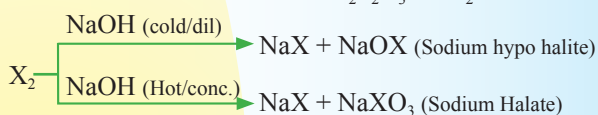
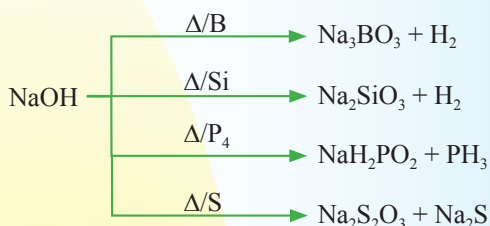
- Na_2CO_3 does not impart any colour to the flame but NaCl does because the thermal ionization of Na_2CO_3 does not take place at the temperature of flame of the burner.

Reaction of NaOH

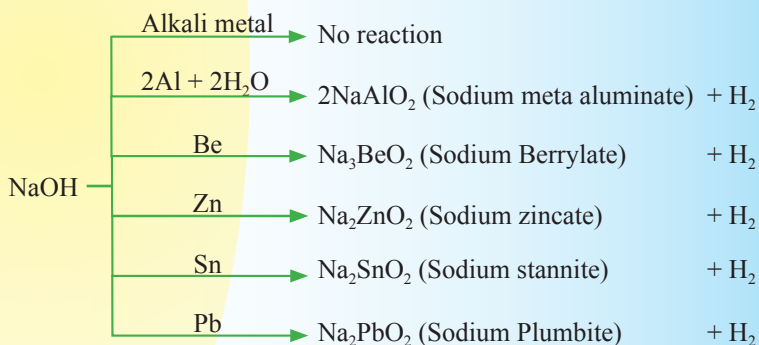
(i) NaOH is strong base.



(ii) **Reaction with non metals** : no reaction with H_2 , N_2 and C



(iii) Reaction with Metal:



ALKALINE EARTH METALS

Physical properties : General electronic configuration ns^2 .

General oxidation state +2.

Atomic/Ionic size $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$

Ionisation energy $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$

Flame Test : Among alkaline earth metals, Be and Mg do not impart any characteristic colour to the flame due to more ionization energy.

Ca - Brick red

Sr - Crimson red

Ba - Apple green

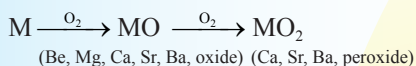
Basic nature increases down to the group

Reducing property: Order of reducing property in aqueous and gaseous medium is

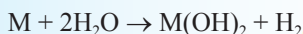


CHEMICAL PROPERTIES

With O₂



With Water



With Air

In moist air, except Be oxide elements converts into carbonates.

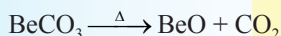
In dry air gives nitride and oxide both

With NH₃

Only Ca, Sr and Ba gives deep blue-black solution of ammoniated electron.

Carbonates

(i) Except BeCO₃, all the carbonates are stable towards heat



(ii) Order of decreasing stability



Nitrates

(i) Alkaline earth metals forms M(NO₃)₂ type nitrates. (M -Alkaline earth metal).

(ii) All alkaline metals nitrates on heating gives oxides and NO₂ + O₂

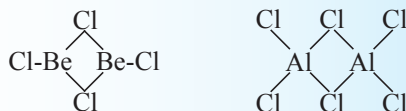


DIAGONAL SIMILARITY BETWEEN BERYLLIUM AND ALUMINIUM

In many of its properties, beryllium resembles Aluminium. Thus

- The two elements have same electronegativity and their charge/ radius ratios.
- Both metals are fairly resistant to the action of acids due to a protective film of oxide on the surface. Both metals are acted upon by strong alkalis to form soluble complexes, beryllates $[\text{Be}(\text{OH})_4]^{2-}$ and aluminates, $[\text{Al}(\text{OH})_4]^-$.

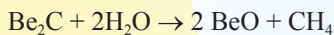
(c) The chlorides of both beryllium and aluminium



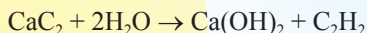
have bridged chloride structures in vapour phase.

(d) Salts of these metals form hydrated ions, Ex. $[\text{Be}(\text{OH}_2)_4]^{2+}$ and $[\text{Al}(\text{OH}_2)_6]^{3+}$ in aqueous solution. Due to similar charges/radius ratios of beryllium and aluminium ions have strong tendency to form complexes. For example beryllium forms tetrahedral complexes such as BeF_4^{2-} and $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$ and aluminium forms octahedral complexes like AlF_6^{3-} and $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$.

- Be_2C on treatment with H_2O forms CH_4 while CaC_2 forms C_2H_2 .



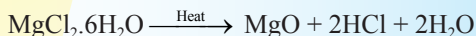
Methane



Acetylene

CHLORIDE OF ALKALINE EARTH METAL

- BeCl_2 in the vapour phase above 900°C is monomeric; below 900°C in the vapour exists as a mixture of monomer BeCl_2 and dimer Be_2Cl_4 , in the solid state, has a polymeric structure and when dissolved in a coordinating solvent it exists as a monomer.
- Anhydrous MgCl_2 cannot be prepared by the simple heating of hydrated magnesium chloride $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, as it gets hydrolysed to magnesium oxide.



- Out of the oxides of group 2 elements only BeO is extremely hard, non volatile, has high melting point and it is amphoteric.

ANALYTICAL DETECTION OF Mg

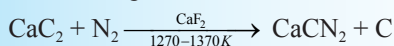
- Charcoal cavity test. On heating on a charcoal cavity with one drop of $\text{Co}(\text{NO}_3)_2$, a pink colour is imparted to the residue $\text{CoO} \cdot \text{MgO}$.
- The salt solution when mixed with NH_4Cl and NH_4OH and finally treated with soluble phosphates forms a white precipitate of magnesium ammonium phosphate.



white ppt.

CALCIUM CYANAMIDE

- Calcium cyanamide (CaCN_2) is prepared by heating a mixture of CaC_2 in an atmosphere of N_2 at 1270-1370K with CaF_2 .



Its trade name is Nitrolim.

- Calcium cyanamide (CaCN_2) is a slow acting manure and is preferred to soluble compounds like NaNO_3 or $(\text{NH}_4)_2\text{SO}_4$ since it confers fertility of a permanent nature. It is a nitrogenous fertiliser and undergoes a series of changes giving cyanamide, urea, NH_3 and finally the nitrates which are assimilable by plants.
- $\text{CaCN}_2 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{NCN}$
- $\text{H}_2\text{NCN} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{NCONH}_2$
Urea
- $\text{H}_2\text{NCONH}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_3$

OXIDE OF CALCIUM

Quick lime (CaO) is obtained when limestone is heated at about 1000°C . On adding water, quick lime gives a hissing sound and forms calcium hydroxide, known as slaked lime. The paste of lime in water is called milk of lime while the filtered and clear solution is known as lime water. Chemically both are $\text{Ca}(\text{OH})_2$.

Quick lime is used for making caustic soda, bleaching powder, calcium carbide, mortar, cement, glass, dye stuffs and purification of sugar.

Mortar: It is a building material. It consists slaked lime and silica in the ratio of 1:3. The mixture made a paste with water. It is called mortar.

PLASTER OF PARIS

- Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) found in nature, when heated, it first changes from monoclinic form to orthorhombic form without loss of water. At 120°C , it loses three-fourth of its water of crystallisation and forms hemihydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$) known as plaster of Paris.
- Plaster of Paris has the property of setting to a hard mass $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, slight expansion occurs during setting addition of alum to plaster of Paris makes the setting very hard. The mixture is known as **Keene cement**.
- Plaster of Paris is used for setting broken or dislocated bones, castes for statues, toys and in dentistry.
- When plaster of Paris is heated at 200°C , it forms anhydrous calcium sulphate which is known as dead plaster. It has no setting property.

Cement

Cement is an important building material. The average composition of portland cement is : CaO 61.5%, SiO₂ 22.5%, Al₂O₃ 7.5%. Cement consists of :

Tricalcium silicate 3CaO.SiO₂

Dicalcium silicate 2CaO.SiO₂

Tricalcium aluminate 3CaO.Al₂O₃

Tetracalcium aluminato - ferrite 4CaO. Al₂O₃. Fe₂O₃

When cement is mixed with water, it sets to a hard mass, this is called setting. Setting is an exothermic process. During setting hydration occurs.

CALCIUM HYDROXYAPATITE

Hydroxyapatite, Ca₉(PO₄)₆. Ca(OH)₂ is the main component of tooth enamel. Cavities are formed when acids decompose this enamel. This can be prevented by converting the hydroxyapatite to more resistant enamel-fluorapatite, Ca₉(PO₄)₆.CaF₂.

HYDROLITH

Hydrolith (CaH₂) is calcium hydride & on hydrolysis for calcium hydroxied & librate hydrogen.



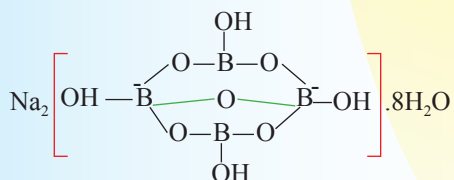
p-Block

13th-GROUP

- Some important ores of Boron are given as under.
 - (i) Boric acid, H_3BO_3
 - (ii) Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
 - (iii) Colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
- Some important minerals of aluminium are given as under.
 - (i) Corundum, Al_2O_3
 - (ii) Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
 - (iii) Cryolite, Na_3AlF_6
 - (iv) Feldspar, KAlSi_3O_8

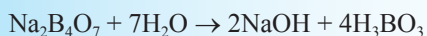
BORAX $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$

$\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$

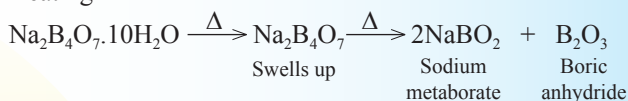


Properties

- (i) It is a white crystalline solid of formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. In fact it contain the tetranuclear units $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and correct formula; therefore, is $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$.
- (ii) Hydrolysis



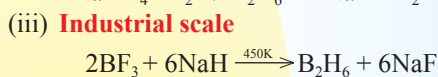
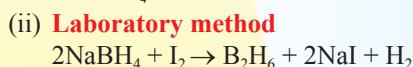
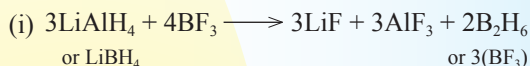
(iii) Heating



(iv) When borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $\text{CO}(\text{BO}_2)_2$ bead is formed.

DIBORANE, B_2H_6

Preparation



Properties

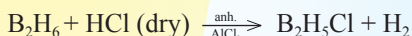
(i) Diborane is a colourless, highly toxic gas with a boiling point of 180 K.

(ii) Diborane catches fire spontaneously upon exposure to air.

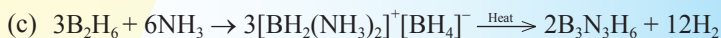
(iii) Reaction with oxygen :



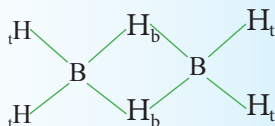
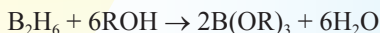
(iv) Hydrolysis :



(v) Reaction with Lewis Bases



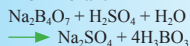
(vi) Reaction with ROH :



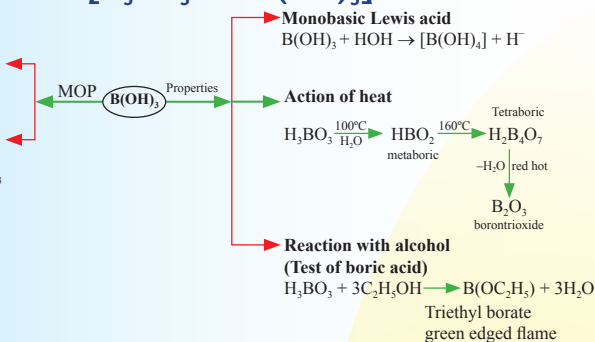
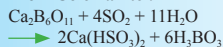
dimer due to formation of 3 centre-2e-bond inorganic benzene.

ORTHOBORIC ACID [H₃BO₃ OR B(OH)₃]

From Borax:

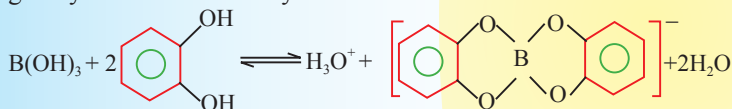


From Colemanite :



Properties:

- Boric acid is a weak monobasic acid
 $\text{B}(\text{OH})_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + [\text{B}(\text{OH})_4]^-$
 $\text{pK}_a = 9.25$
- It is difficult to titrate boric acid against NaOH solutions and the end point cannot be located correctly. However, it can be successfully titrated in the presence of polyhydroxy alcohols (e.g. Glycerol, mannitol, catechol or sugar). The presence of these compounds greatly increase the acidity of boric acid.

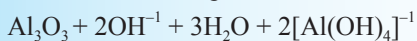


Boron is complex by these compounds. These complex ions cannot interact with H⁺ ions as boron atom has already acquired its maximum covalency of four. Consequently, boric acid in presence of polyhydroxy alcohols can be titrated against NaOH to a definite end point.

EXTRACTION OF ALUMINIUM

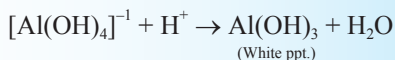
Al is usually extracted from Bauxite, Al₂O₃·2H₂O. First, bauxite is purified from the impurities (Red bauxite contains Fe₂O₃) as impurity, while white bauxite contains silica as impurity). Red bauxite can be purified by Baeyer's process or Hall's process, while white bauxite is purified by Serpeck's process.

- Baeyer's process**, involves the roasting of the ore to convert FeO to Fe₂O₃ and then digested at 423K with conc. NaOH solution for a few hours when Al₂O₃ gets dissolved to give a solutions of [Al(OH)₄]⁻. The basic oxide impurities such as Fe₂O₃ are not affected.



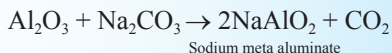
Aluminate ion

Fe₂O₃ left undissolved is filtered off. The treatment of [Al(OH)₄]⁻ solution with a weak acid precipitate pure Al(OH)₃.

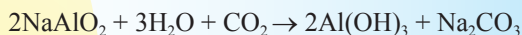


The Al(OH)₃ precipitate is removed by filtration and ignited to get alumina, Al₂O₃.

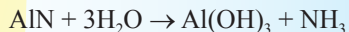
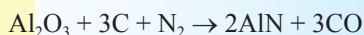
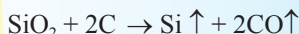
- **Hall's process** involves the fusion of the ore with Na₂CO₃ when soluble sodium meta aluminate, NaAlO₂ is produced. This is extracted with water when Fe₂O₃ is left as a residue.



The water extract is heated upto 333K and CO₂ is passed through it. Al(OH)₃ is precipitated due to hydrolysis and is ignited to get alumina, Al₂O₃.



- **Serpeck's process** involves the heating of bauxite with coke in a current of N₂ at 2075K. The SiO₂ present in the ore is reduced to silicon which volatilizes off and alumina gives aluminium nitride. This can be hydrolysed to Al(OH)₃ which on fusion gives alumina.



Aluminium nitride

Electrolysis of Al₂O₃ to form aluminium. Pure alumina is dissolved in fused cryolite, Na₃AlF₆ at 1225 K by current of 100 amp eres and 6-7 voltsto get Al. The Al obtained is purified by Hoopes process.

ALUMINIUM TRIFLUORIDE

- **Aluminium trifluoride** (AlF₃) is different from other trihalides of Al in being insoluble and nonvolatile in nature. In AlF₃ each Al is surrounded by a distorted octahedron of 6F atoms and 1 : 3 stoichiometry is achieved by the sharing of corner fluorine atoms between two octahedral.

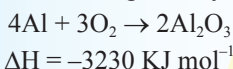
ALUMINIUM CHLORIDE

- Aluminium chloride (AlCl₃) in the pure and anhydrous state is a white solid but commercial samples are yellowish due to the impurity of FeCl₃.
- Anhydrous AlCl₃, in the crystalline state possesses a closely packed layer structure with six coordinated aluminium octahedral arrangement.

- Anhydrous AlCl_3 has a very high affinity for water. On treating AlCl_3 with water, the Cl^- ions go outside the coordination sphere to form $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ with enthalpy of solution -300 KJ mol^{-1} . Due to this strong Al – O linkage hydrate cannot be dehydrated on heating to form AlCl_3 .

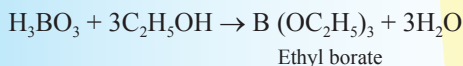


- Aluminium chloride, is a polymeric solid which exists as a dimer Al_2Cl_6 between $200\text{--}400^\circ\text{C}$ and then monomer up to 800°C .
- **Thermite welding**, Aluminium has got a very high affinity for oxygen.



It, therefore, displaces metals less electropositive than itself from oxides. The large amount of heat produced is used in welding rails or heavy machinery without removing them from their position. This is called thermite welding or Gold Schmidt's aluminothermic process. In this process, a mixture of Ferric oxide (3 parts) and aluminium powder (1 part) called thermite is used.

- **Boron nitride** (BN), has a structure similar to that of graphite.
- Green edged flame test for borate (BO_3^{3-}) ion. A mixture of $\text{C}_2\text{H}_5\text{OH}$ and BO_3^{3-} salt with conc. H_2SO_4 burns with green edge flame due to the formation of ethyl borate.

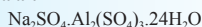


- **Charcoal cavity test for aluminium.** On heating with Na_2CO_3 and a drop of cobalt nitrate solution a blue coloured residue to **cobalt metaaluminate** (Thenard's blue) is obtained.

ALUMS $[\text{M}_2\text{SO}_4 \cdot \text{M}_2'(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}]$

| |
|--|
| Alums are the double salt of Type $[\text{M}_2\text{SO}_4 \cdot \text{M}_2'(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}]$ |
| M : Monovalent Cation: $\text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$ |
| M' : Trivalent Cation: $\text{Al}^{3+}, \text{Fe}^{3+} \text{ \& } \text{Cr}^{3+}$ |

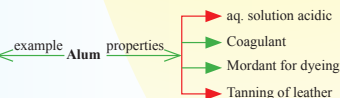
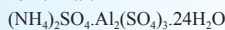
Soda alum



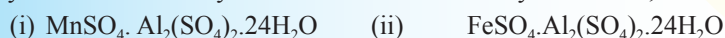
Potash alum



Ammonium alum



Pseudo alums are double sulphates of a divalent and a trivalent metals which crystallize with twenty four water molecules of crystallization, for example.



They are not isomorphous with true alums.

14th-GROUP ELEMENTS

1. The common oxidation exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states.
2. Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).
3. Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.
4. SiO only exists at high temperature.
5. The dioxides CO_2 , SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.
6. Tin decomposes steam to form dioxide and dihydrogen gas.
7. All halide of 14th group are covalent. Exceptions are SnF_4 and PbF_4 , which are ionic in nature.
8. Stability of dihalides increases down the group.
9. The order of catenation is $\text{C} \gg \text{Si} > \text{Ge} \approx \text{Sn}$. Lead does not show catenation.
 - Catenation is the unique tendency of 14 group elements to form long chains of different sizes and shapes. The tendency to show catenation is directly related to the strength of bond. The bond energies of 14 group elements decrease as under :

| | C-C | Si-Si | Ge-Ge | Sn-Sn | Pb-Pb |
|--------------------------------------|-----|-------|-------|-------|-------|
| Bond energy (kJ mole ⁻¹) | 348 | 222 | 167 | 155 | - |

This is the reason why carbon forms many chains, Si, a few and Ge and Sn form practically no chains.

- CO_2 is a gas while SiO_2 is a solid at room temperature.
- SiO only exists at high temperature.
- CO_2 , SiO_2 , GeO_2 , GeO are acidic, PbO, PbO_2 is SnO and SnO_2 are amphoteric an CO is neutral
 - \Rightarrow Among 14th group element only Sn reacts with steam to produce H_2 gas.
 - \Rightarrow Tetrahalide of 14th group elements are covalent except SnF_4 and PbF_4 .

Stability of oxidationstate

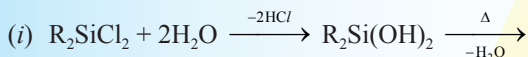
- $\Rightarrow \text{C}^{+4} \rightarrow \text{Pb}^{+4}$ (Stability)
- $\Rightarrow \text{C}^{+2} \rightarrow \text{Pb}^{+2}$ (Stability)
- $\Rightarrow \text{Pb}^{+4}$ compounds are strong oxidizing agent.
- $\Rightarrow \text{PbI}_4$ does not exist.

- Trimethylamine (CH₃)₃N is pyramidal while Trisilylamine N(SiH₃)₃ is planar due to back bonding.

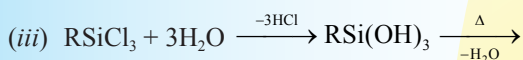
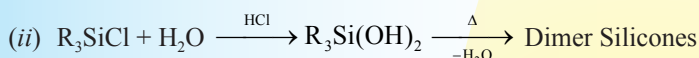
SILICONES (ORGANO SILICONE POLYMER)

- Silicones are polymeric organosilicon compounds containing Si–O–Si linkage. They have high thermal stability of Si–O–Si chains and are also called high temperature polymers.

General formula : (R₂SiO)_n. Where R = –CH₃, –C₂H₅, –C₆H₅



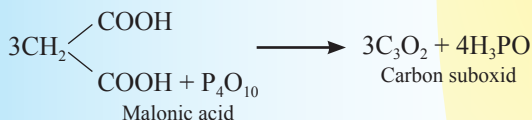
Linear Silicones/Cyclic Silicones



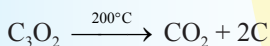
Crossed Linked Silicones

CARBON SUBOXIDE

- Carbon suboxide (C₃O₂) is a foul smelling gas which can be prepared by the dehydration of malonic acid with P₄O₁₀.



On heating upto 200°C, it decomposes into CO₂ and carbon.

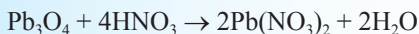


The molecule is thought to have a linear structure.



OXIDE OF LEAD

- **Red lead (Pb₃O₄)** is considered to be mixture of lead monoxide and lead dioxide and it is written as (PbO₂·2PbO).
- **Lead dioxide (PbO₂)**. It is a brown powder obtained by the treatment of red lead with HNO₃.



It is used as an active material of the positive plate in storage cells and finds use in match industry as an oxidizing agent.

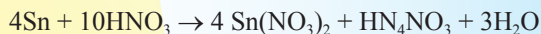
REACTION OF LEAD OXIDES

| Oxide | ex NaOH | HCl | H ₂ SO ₄ | HNO ₃ |
|--------------------------------|---|-------------------------------------|------------------------------------|--|
| PbO | Na ₂ PbO ₂ | PbCl ₂ | PbSO ₄ | Pb(NO ₃) ₂ |
| PbO ₂ | Na ₂ PbO ₃ | PbCl ₂ + Cl ₂ | PbSO ₄ + O ₂ | Pb(NO ₃) ₂ |
| Pb ₂ O ₃ | Na ₂ PbO ₂ + NaPbO ₃ | PbCl ₂ + Cl ₂ | PbSO ₄ + O ₂ | Pb(NO ₃) ₂ + PbO ₂ |
| Pb ₃ O ₄ | Na ₂ PbO ₂ + Na ₂ PbO ₃ | PbCl ₂ + Cl ₂ | PbSO ₄ + O ₂ | Pb(NO ₃) ₂ + PbO ₂ |

Tin and Its Compound

- **Action of conc. HNO₃ on tin**

(a) Dilute HNO₃



(b) Hot conc. HNO₃



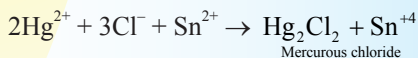
Metastannic acid

- **Action of conc. NaOH on tin**

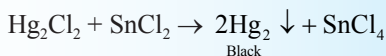


SnCl₂

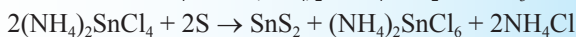
- SnCl₂·2H₂O on heating undergoes to form its basic chloride Sn(OH).Cl. The anhydrous salt, therefore, be obtained by heating the hydrated salt in the presence of HCl vapour.
- Stannous chloride reduces mercuric chloride (HgCl₂) to a white precipitate of mercurous chloride (Hg₂Cl₂)



which finally turns to metallic mercury (dark grey or black)



- **Mosaic gold (SnS₂):** Stannic sulphide exists in yellow glistening scales which is used for decorative purposes under and the name mosaic gold. It is prepared by heating mixture of tin fillings, sulphur and NH₄Cl in a retort.



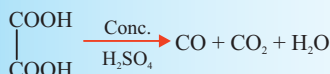
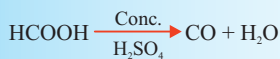
- **Tin Cry.** Tin metal when bent produces a cracking noise due to rubbing of metal crystals over one another.

CARBON MONOXIDE [CO]

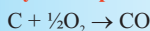
Colorless odourless, tasteless, neutral, poisonous gas



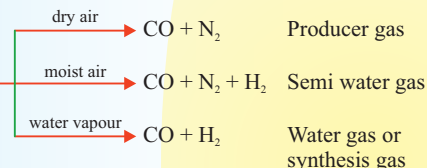
By dehydration of formic acid and oxalic acid



By incomplete combustion

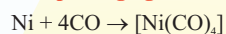


By passing air on red hot coke

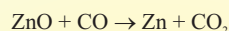
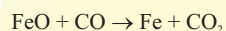


MOP **CO** properties

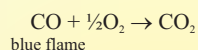
Complexing agent



Reducing agent

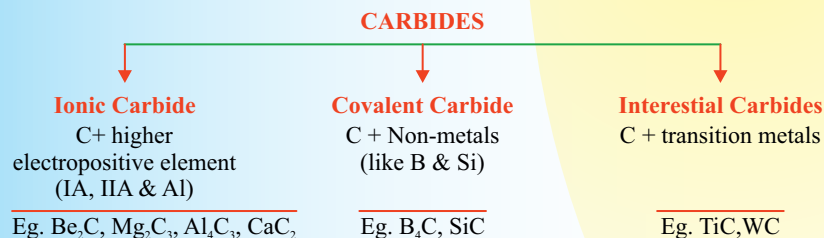


Combustion



CARBIDES

Binary compounds of carbon with other elements (except hydrogen) are known as carbides



15th-GROUP ELEMENTS

Nitrogen Family

1. Nitrogen and phosphorus are **non-metals**, arsenic and antimony **metalloids** and bismuth is a **typical metal**.
2. Except nitrogen all the elements show allotropy.
3. Bismuth hardly forms any compound in -3 oxidation state.
4. The only well characterised Bi (V) compound is BiF_5 .

5. In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. for example,



6. In case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid.

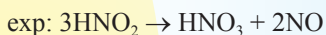
7. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.

8. In case of nitrogen, only NF_3 is known to be stable.

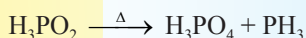
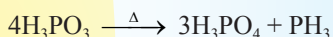
9. Trihalides except BiF_3 are predominantly covalent in nature.

⇒ The only well characterised Bi (V) compound is BiF_5 .

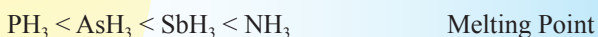
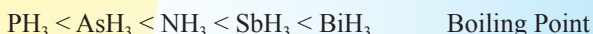
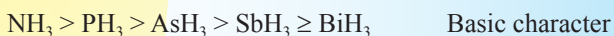
⇒ All the oxidation states from +1 to +4 tend to disproportionate in acidic solution :



⇒ All the intermediate oxidation states disproportionate into +5 and -3



⇒ Hybride of 15th group elements:



⇒ Penta oxide of 15th group element is acidic. N_2O_5 , P_2O_5 are acidic, As_2O_5 , Sb_2O_5 are amphoteric with Bi_2O_5 is basic.

⇒ Trihalide of 15th group elements are covalent except BiF_3

Structure of Oxides of Nitrogen and Phosphorus Nitrogen

| Oxide of Nitrogen | Oxide State | Physical Appearance | Structure |
|------------------------------------|-------------|---------------------|---|
| N_2O nitrous oxide | +1 | Colourless gas | $\text{N} \equiv \text{N} \rightarrow \text{O}$ |
| NO Nitric oxide | 2 | Colourless gas | $\text{N} = \text{O}$ |

| Oxide of Nitrogen | Oxide State | Physical Appearance | Structure |
|---|-------------|---------------------|-----------|
| N ₂ O ₃ Dinitrogen trioxide | +3 | Blue colour solid | |
| N ₂ O ₄ Dinitrogen tetroxide | +4 | Colourless solid | |
| NO ₂ Nitrogen dioxide | +4 | Brown gas | |
| N ₂ O ₅ Dinitrogen pentaoxide | +5 | Colourless solid | |

Oxides of Nitrogen

| Name | Formula | Oxidation state of nitrogen | Common methods of preparation | Physical appearance and chemical nature |
|---|-------------------------------|-----------------------------|--|---|
| Dinitrogen oxide [Nitrogen oxide] | N ₂ O | +1 | $\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$ | Colourless gas, neutral |
| Nitrogen monoxide [Nitrogen (II) oxide] | NO | +2 | $2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$ | Colourless gas, neutral |
| Dinitrogen trioxide [Nitrogen (III) oxide] | N ₂ O ₃ | +3 | $2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{ K}} 2\text{N}_2\text{O}_3$ | Blue solid, acid blue liquid (-30°C) |
| Nitrogen dioxide [Nitrogen (IV) oxide] | NO ₂ | +4 | $2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{ K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$ | Brown gas, acidic |
| Dinitrogen tetroxide [Nitrogen (IV) oxide] | N ₂ O ₄ | +4 | $2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{Cool}} \text{N}_2\text{O}_4$ | Colourless solid/liquid, acidic |

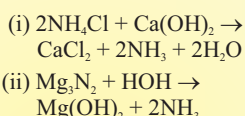
| Name | Formula | Oxidation state of nitrogen | Common methods of preparation | Physical appearance and chemical nature |
|---|-------------------------------|-----------------------------|--|---|
| Dinitrogen pentaoxide [Nitrogen (V) oxide] | N ₂ O ₅ | +5 | 4HNO ₃ + P ₄ O ₁₀ → 4HPO ₃ + 2N ₂ O ₅ | Colourless solid, acidic |

COMPOUNDS OF NITROGEN FAMILY

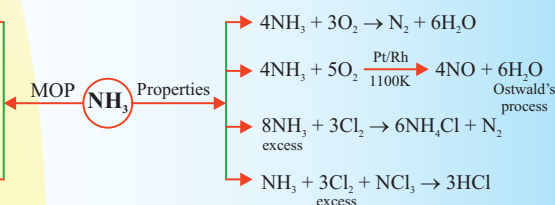
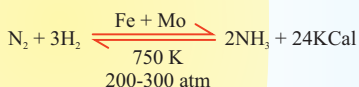
Ammonia (NH₃)

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

Preparation



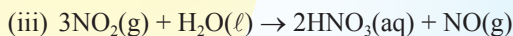
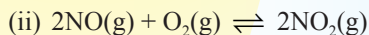
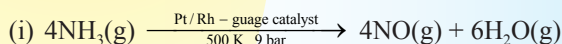
Manufacturing Haber Process



Nitric Acid (HNO₃)

Preparation

Ostwald's process



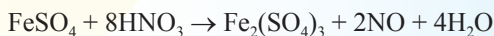
Properties

HNO₃, nitric acid was earlier called as aqua fortis (meaning strong water).

It usually acquires yellow colour. Due to its decomposition by sunlight into NO₂.

It acts as a strong oxidising agent.

Reaction with FeSO₄

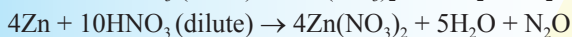
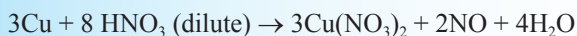


Reaction with non-metals

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

$\text{HNO}_3 \cdot \text{NO}_2$ 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.

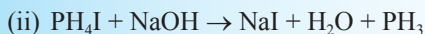
Reaction with metals



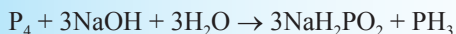
| Concentration of nitric acid | Metal | Main products |
|------------------------------|--------------------|--|
| Very Dilute HNO_3 | Mg, Mn | H_2 + metal nitrate |
| | Fe, Zn, Sn | NH_4NO_3 + metal nitrate |
| | Cu, Ag, Hg | No reaction |
| Dilute HNO_3 | Fe, Zn | N_2O + metal nitrate |
| | Pb, Cu, 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



Laboratory preparation



Uses

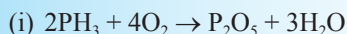
As Holme's signals in deep seas and oceans.

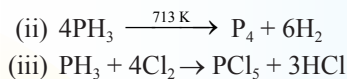
For the production of smoke screens.

Physical properties

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

Chemical properties

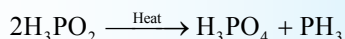
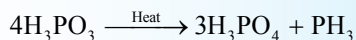




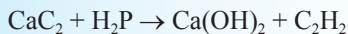
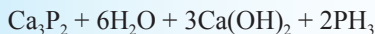
Oxoacids of Phosphorus

| Name | Formula | Oxidation state of nitrogen | Characteristic bonds and their number | Preparation |
|-------------------------------|-------------|-----------------------------|--|---|
| Hypophosphorus (Phosphinic) | H_3PO_2 | + 1 | One P — OH | white P_4 + alkali |
| Orthophosphorous (Phosphonic) | H_3PO_3 | + 3 | Two P — OH One P — H One P = O | $P_2O_3 + H_2O$ |
| Pyrophosphorous | $H_4P_2O_5$ | + 3 | Two P — OH Two P — H Two P = O | $PCl_3 + H_3PO_3$ |
| Hypophosphoric | $H_4P_2O_6$ | + 4 | Four P — OH Two P = O One P — P | red P_4 + alkali |
| Orthophosphoric | H_3PO_4 | + 5 | Three P — OH One P = O | $P_4O_{10} + H_2O$ |
| Pyrophosphoric | $H_4P_2O_7$ | + 5 | Four P — OH Two P = O One P — O — P | heat phosphoric acid |
| Metaphosphoric* | $(HPO_3)_n$ | + 5 | Three P — OH Three P = O Three P — O — P | phosphorous acid + Br_2 , heat in a sealed tube |

- Acidity of oxides and the solubility of 15 group oxides decreases from N to Bi. For example, N_2O_3 , N_2O_5 , P_4O_6 , P_4O_{10} , As_4O_{10} are acidic and dissolve water forming acids. Sb_4O_6 and Sb_4O_{10} are weakly acidic and insoluble in water Bi_2O_3 is a basic oxide and is insoluble in water.
- On heating, phosphorus acid, H_3PO_3 decomposes into phosphine (PH_3) and phosphoric acid (H_3PO_4).

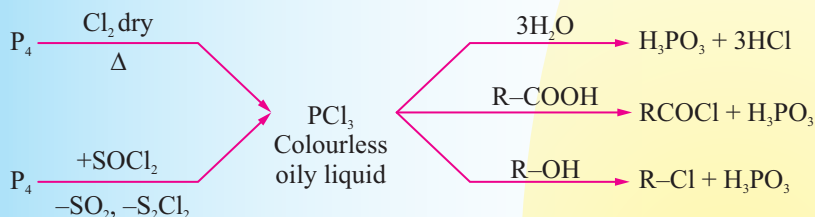


- **Holme's signals:** A mixture of Ca_3P_2 and CaC_2 on treatment with H_2O forms PH_3 and P_2H_4 along with C_2H_2 . The mixture burns with a bright

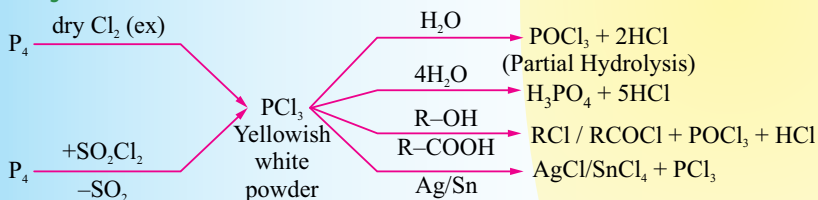


- Smoke screens, involve the use of calcium phosphide, Ca_3P_2 . The PH_3 gas obtained from Ca_3P_2 catches fire to give the needed smoke.
- **Phosphatic slag or Thomas slag or Basic slag** is obtained as a byproduct in the manufacture of steel and is probably a double salt of tricalcium phosphate and calcium silicate.

PCl_3



PCl_5



16th-GROUP ELEMENTS

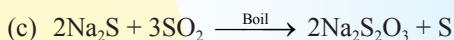
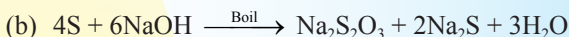
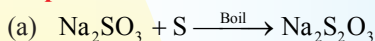
Oxygen Family

1. Oxygen is the most abundant of all the elements on earth crust.
2. Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal.
3. Polonium hardly shows -2 oxidation state.
4. Reducing property of dioxide decreases from SO_2 to TeO_2 , SO_2 is reducing while TeO_2 is an oxidising agent.
5. Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons.
6. The well known monohalides are dimeric in nature. Examples are S_2F_2 , S_2Cl_2 , S_2Br_2 , Se_2Cl_2 and Se_2Br_2 . These dimeric halides undergo disproportionation as given below : $2\text{Se}_2\text{Cl}_2 \rightarrow \text{SeCl}_4 + 3\text{Se}$

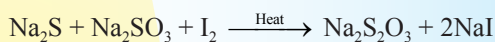
- The weakening of M–H bond with the increase in the size of M (not the electronegativity) explains the increasing acidic character of hydrides down the group.
- **Halides** : All these elements form a number of halides. The halides of oxygen are not very stable. Selenium doesn't form dihalides.
e.g. OF₂, Cl₂O₆, I₂O₅, etc.

SODIUM THIOSULPHATE Na₂S₂O₃·5H₂O

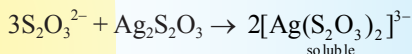
• Preparation



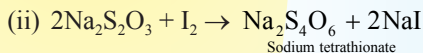
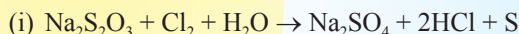
(d) Spring's reaction



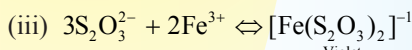
- **Concentrated Na₂S₂O₃** does not give a white ppt. with AgNO₃. This is because silver thiosulphate formed is readily soluble in excess of sodium thiosulphate forming soluble complex.



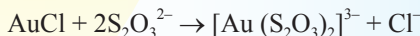
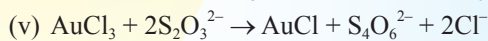
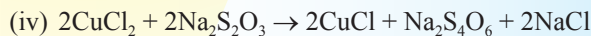
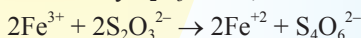
Reaction with oxidizing agent



This reaction forms the basis of iodometric estimation of Cr₂O₇²⁻ and Cu²⁺ salts.

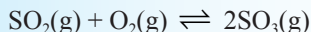


The violet colour disappears quickly due to the reduction of ferric chloride by S₂O₃²⁻ ions,

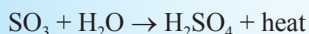


- **Sulphur trioxides** (SO₃) is a white crystalline solid with melting point 290 K and boiling point 318 K.
- SO₃ is prepared by the direct oxidation of SO₂ with atmospheric oxygen in presence of finely divided Pt or V₂O₅ at a pressure of 2 bar and temperature 720 K.

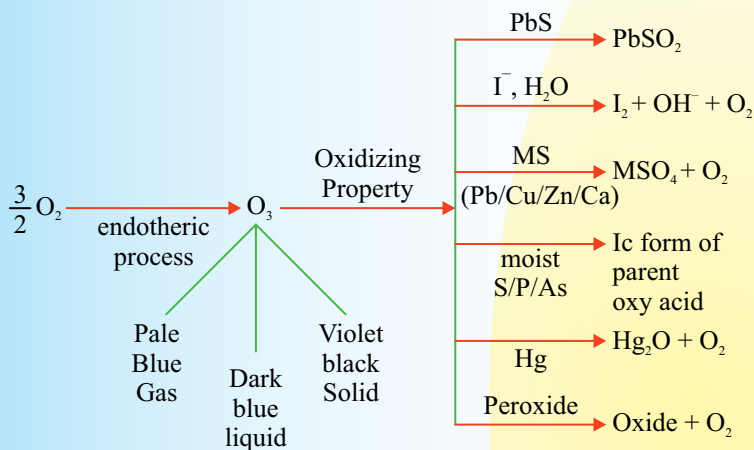
- SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.



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



OZONE

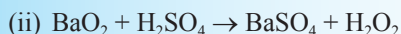


* Fishy odour, Highly toxic.

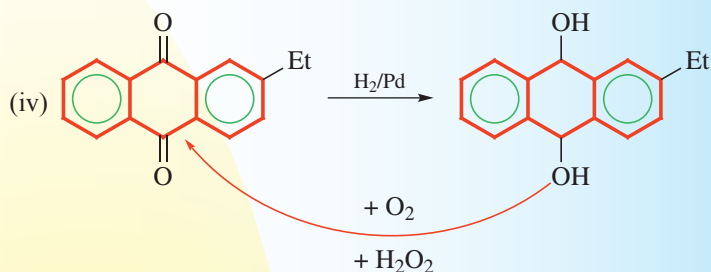
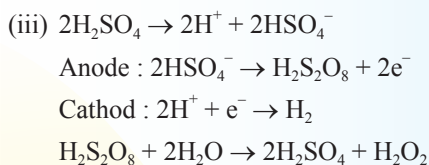
| Gases | Absorbent |
|-----------------|---------------------------------|
| O ₃ | Turpentine Oil/Oil of cinnamon. |
| NO | FeSO ₄ |
| SO ₂ | NaOH |
| CO | Cu ₂ Cl ₂ |
| O ₂ | Pyrogalol |

HYDROGEN PEROXIDE

Preparation

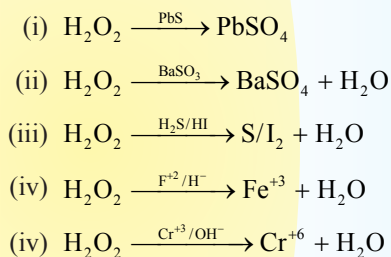


(Now a day conc. H_3PO_4 is used)

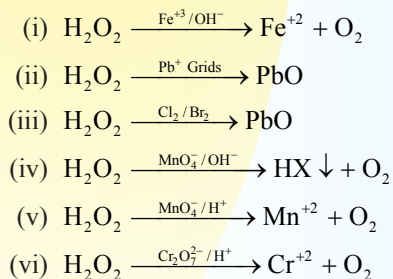


Properties

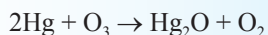
Oxidizing Property



Reducing Property



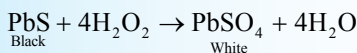
- Tailing of mercury is due to the formation of mercury oxide when Hg reacts with ozone.



As a result of it, mercury loses its meniscus and starts sticking to the glass.

- The bleaching action of Ozone and H_2O_2 is permanent and is due to oxidation while that of SO_2 is temporary and is due to reduction.

- H_2O_2 is used to restore the colour of old lead paintings which have been blackened due to the formation of PbS by the action of H_2S present in the air.



- Antichlor action H_2O_2 is due to its tendency to reduce the excess of chlorine from bleaching powder to HCl .
 - $\Rightarrow \text{NH}_2 \cdot \text{NH}_2 + \text{H}_2\text{O}_2$ as rocket propellant.
 - \Rightarrow Storage:

SULPHURIC ACID (H_2SO_4)

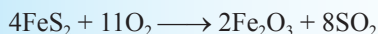
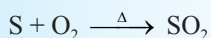
It is also known as oil of vitriol and king of chemicals.

Manufacture of sulphuric acid

Lead chamber process

The various steps involved are :

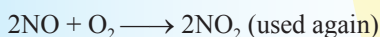
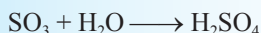
- (a) Production of SO_2 : By burning S or iron pyrites.



- (b) Production of catalyst : Oxides of nitrogen.



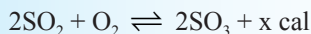
- (c) Reaction in lead chamber



Contact process

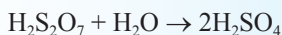
The steps involved are:

- (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 .



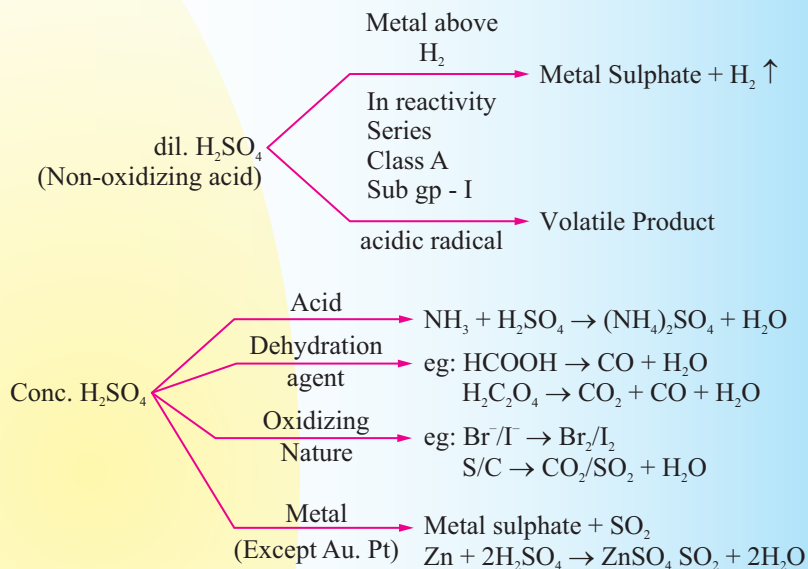
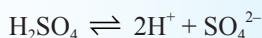
Catalyst : Formerly, platinised asbestos was used which is costly and easily poisoned. These days V_2O_5 is used.

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



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

It is strong dibasic acid.



Uses :

In lead storage batteries.

In manufacture of paints and pigments.

In metallurgy for electrolytic refining of metals.

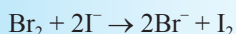
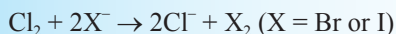
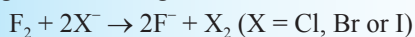
17th–GROUP ELEMENTS

- The electron affinity values (in KJ mol^{-1}) for 17 group element are given below:

| | | | |
|-----|-----|-----|-----|
| F | Cl | Br | I |
| 333 | 349 | 325 | 296 |

- 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.
- 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 $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

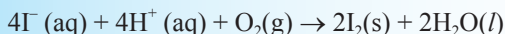
4. In general, a halogen oxidises halide ions of higher atomic number.



5. Reaction with water :



(where X = Cl or Br)



6. Halogens form many oxides with oxygen but most of them are unstable.

7. Fluorine forms two oxides OF_2 and O_2F_2 . However, only OF_2 is thermally stable at 298 K.

These oxides are essentially oxygen fluoride because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents.

8. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.

9. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, $\text{I} > \text{Cl} > \text{Br}$.

10. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

Reactivity : All halogens are chemically very reactive elements. This is due to their low dissociation energy and high EN. Fluorine is the most reactive and iodine is the least reactive halogen.

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

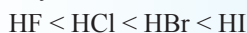
AB_7 type : IF_7

HYDROGEN HALIDES

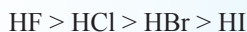
Bond strength, bond length and thermal stability :

- Since size of halogen atom increases from F to I down the group, bond length of H – X bond increases down the group.

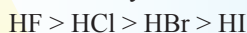
∴ reactivity and acidic character ↑.



- Bond strength is inversely, proportional to bond length i.e., larger the bond length, lower the bond strength is

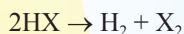
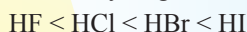


- Higher the bond dissociation energy greater will be thermal stability. Thus, thermal stability follows the order.



REDUCING CHARACTER

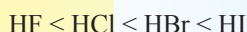
The reducing character of hydrogen halides increases down the group as



A less thermally stable compound has more tendency to release hydrogen easily and show greater reducing property.

ACIDIC STRENGTH

The acidic strength of these acids increases down the group and hence follows the order.

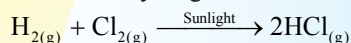


Since H–I bond is weakest, it can be easily dissociated into H^+ and I^- ions while HF with greater bond dissociation energy can be dissociated with maximum difficulty.

HYDROCHLORIC ACID, (HCl)

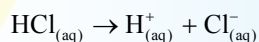
Preparation : By dissolving hydrogen chloride gas in water. Hydrogen chloride gas required in turn can be prepared by the following methods:

By the direct combination of hydrogen and chlorine.



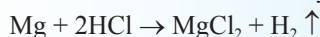
Hydrogen chloride gas can also be obtained by burning hydrogen in chlorine.

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



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

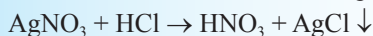
Metal + Hydrochloric → Metal chloride + Hydrogen



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



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



Reducing property : HCl is a strong reducing agent.



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 group which show certain characteristics of halide ions. For example Cyanide (CN⁻), Cyanate (OCN⁻), Thiocyanate (SCN⁻), Selencyanate (SeCN⁻), Azide (N₃⁻), Aziothnio carbonate (SCSN₃⁻) and isocyanate (ONC⁻).

CHLORINE (Cl₂)

Preparation : By oxidation of conc. HCl.



Manufacture :

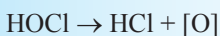
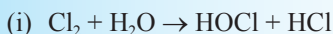
Weldon's process : By heating pyrolusite with conc. HCl.



Deacon process : $2\text{HCl} + \text{O}_2 \xrightarrow{\text{CuCl}_2} \text{Cl}_2 + \text{H}_2\text{O}$

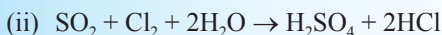
Properties : It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as chlorine water which on careful cooling gives chlorine hydrate Cl₂·8H₂O.

Bleaching action and oxidising property

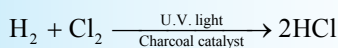


Coloured matter + nascent : [O] → Colourless matter

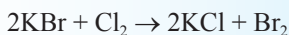
The bleaching action of chlorine is permanent and is due to its oxidising nature.



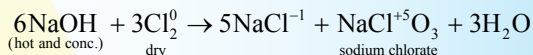
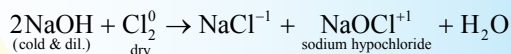
Action of hydrogen :



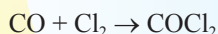
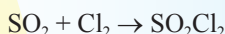
Displacement reactions :



Action of NaOH :



Addition reactions :



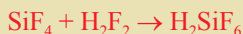
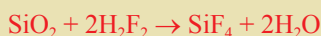
• **Test for chlorine :**

- It is a greenish yellow gas with irritating smell.
- It turns starch iodide paper blue.
- It bleaches litmus paper and indigo solution.



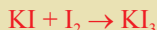
NOTES

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



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 .



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

OXY-ACID

- The acidic strength of the oxoacids of halogen decreases in the following order.



The chlorine oxyanion in which the central atoms has highest oxidation number will have maximum number of oxygen atoms

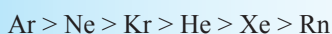
for participation in the extension of the π -bond. Thereby the charge on the ion is delocalized which greatly stabilizes the ion and thus decreases its tendency to accept a proton i.e., causes the ion to be very weak base with the result that the strength of the acid increases.

- The acidity of oxoacids of different halogens having the same oxidation number decreases with the increases in atomic numbers of the halogen

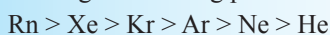


18th-GROUP ELEMENTS

1. Relative Abundance :



2. Melting and Boiling point :

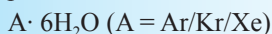


3. He has the lowest boiling point among all element.

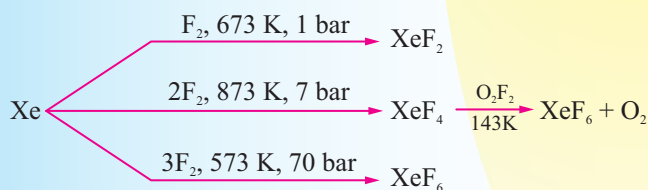
4. Noble gases are monoatomic, colourless, odourless, sparingly soluble in water and diffusing through most commonly used laboratory materials.

5. $\text{O}_2[\text{PtF}_6]$ is the first noble gas compound.

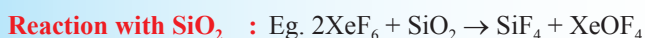
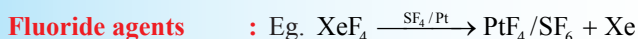
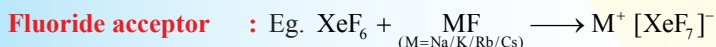
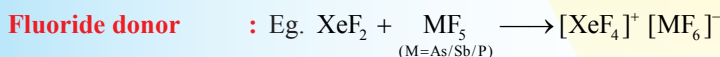
6. Ar, Kr and Xe form clathrate compound when pass in ice with high pressure.



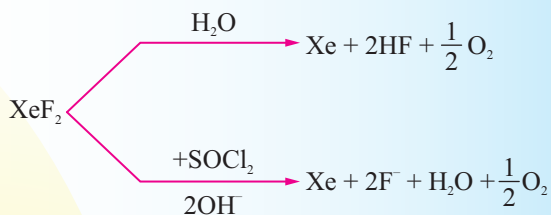
Preparation of Xe-Fluoride



Properties



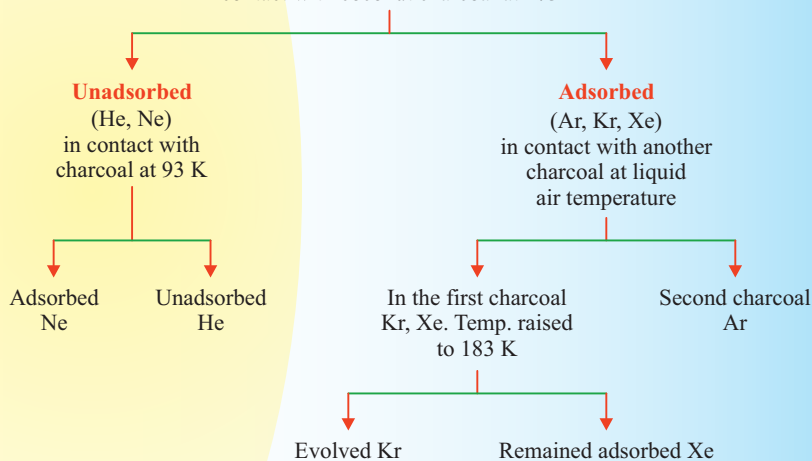
Hydrolysis



NOBLE GAS

In Dewar's method, the separation of noble gases is summarized below:

Mixture of noble gases (He, Ne, Ar, Kr, Xe)
in contact with coconut charcoal at 173 K



The viscosity of He is extremely low, about $1/100^{\text{th}}$ of hydrogen gas.

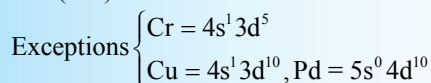
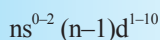


d-Block Transition Elements

DEFINITION

Transition elements are those d-block elements which has 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 but not transition elements.

GENERAL ELECTRONIC CONFIGURATION



TRANSITION SERIES

| | | | |
|-----------------|-----------|--|------------|
| 1 st | 3d series | Sc ₂₁ — Zn ₃₀ | 9 + 1 = 10 |
| 2 nd | 4d series | Y ₃₉ — Cd ₄₈ | 9 + 1 = 10 |
| 3 rd | 5d series | La ₅₇ , Hf ₇₂ — Hg ₈₀ | 9 + 1 = 10 |
| 4 th | 6d series | Ac ₈₉ , Unq ₁₀₄ — Uub ₁₁₂ | 9 + 1 = 10 |

ATOMIC RADIUS

3d series Sc > Ti > V > Cr > Mn ≥ Fe ≈ Co ≈ Ni < Cu < Zn

In a group 3d to 4d series increases but 4d and 5d series nearly same due to poor shielding of f electron. (Lanthanide contraction)

$$3d < 4d \approx 5d$$

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

Melting point: s-block metals < d-block metals

In a series on increasing number of unpaired e⁻ melting point increases upto Cr then decreases.



Half filled d⁵

∴ weak metallic bond



Fully filled d¹⁰

∴ weak metallic bond

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

E.N. Exception Zn < Cd < Hg

Density: s-block metals < d-block metals.

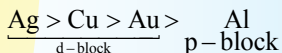
3d series



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 liquid

Electrical conductor



OXIDATION STATE

Transition elements exhibit variable oxidation state due to small energy difference of ns and (n-1)d electrons.

- Sc(+3) and Zn(+2) exhibit only one oxidation state.
- Common oxidation state is +2 & +3
- In 3d series highest oxidation state is +7 (Mn)
- In d-block series highest oxidation state is +8 (Os, Ru)
- In carbonyl compound oxidation state of metals is zero due to synergic effects.
- Their higher oxidation states are more stable in fluoride 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 MnF₄ while oxide is Mn₂O₇

- ⇒ Mn show maximum number of oxidation state (+2 to +7) among 3d series.
- ⇒ Beyond Mn, trihalide are not observe except FeX_3 ($X = \text{Cl}/\text{Br}/\text{I}$) & 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
 $\text{CuI}_2 \longrightarrow \text{CuI} + \frac{1}{2}\text{I}_2$
- ⇒ In aqueous, Cu^+ disproportionated 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 gp $\text{Mo}(+6)$ & $\text{W}(+6)$ are more stable than $\text{Cr}(+6)$

MAGNETIC PROPERTY

All transition elements are paramagnetic due to presence of unpaired electrons. They attract when magnetic field is applied. Magnetic moment of unpaired electron is due to spin and orbital angular momentum.

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

- 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 element and ions having d^0 and d^{10} configuration are diamagnetic.

COLOUR

Colour in transition metal ions is associated with d-d transition of unpaired electron from t_{2g} to e_g set of energies. This is achieved by absorption of light in the visible spectrum, rest of the light is no longer white.

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 mix with other metals form semisolid amalgam except Fe, Co, Ni, Pt.

Interstitial compound

When less reactive nonmetals of small atomic size eg. H, B, N, C, trapped in the interstitial space of transition metals, interstitial compounds are formed, like :- TiC, Mn₄N, Fe₃H etc.

They are nonstoichiometric compounds.

They have high melting point than metals.

They are chemically inert.

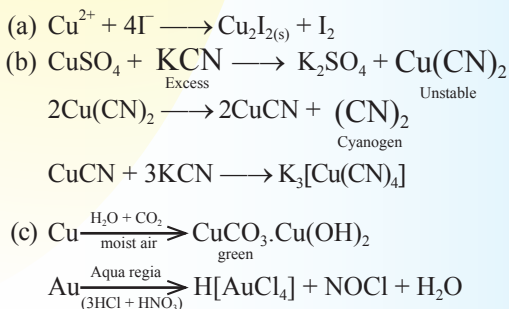
CATALYTIC PROPERTIES

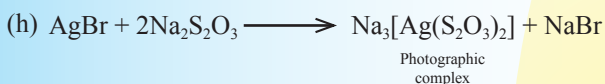
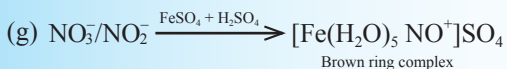
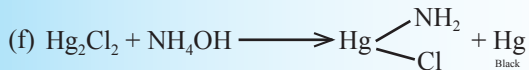
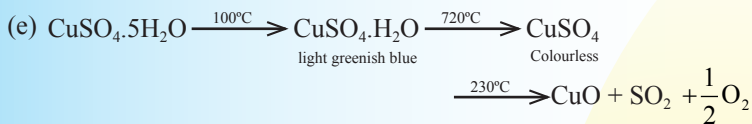
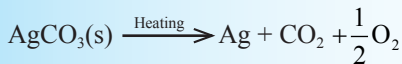
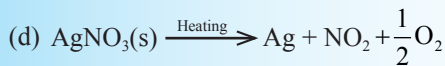
Most of the d-block compounds act as catalyst due to their variable oxidation state or complex formation tendency or adsorption on their surface.

Example:

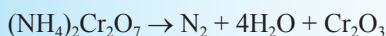
Contact process = V₂O₅
Haber process = Fe₂O₃ + Al₂O₃ + K₂O
Fenton's reagent = FeSO₄ + H₂O₂
Decomposition of KClO₃ = MnO₂
Ostwald process = Pt/Rh
Zeigler Natta = TiCl₄ + (C₂H₅)₃Al
Hydrogenation of Alkene = Ni/Pd
Wilkinson's catalyst = RhCl + PPh₃

Important reactions of d-block elements

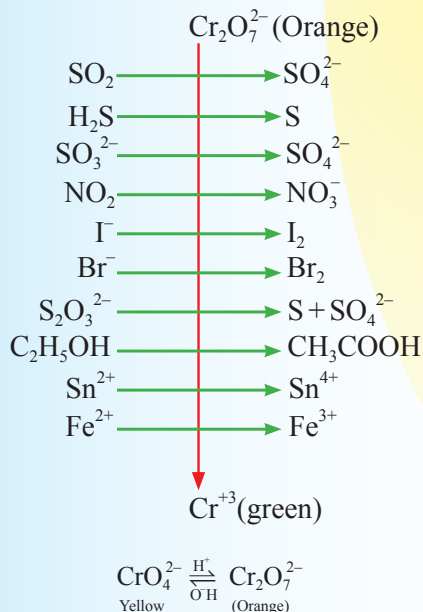


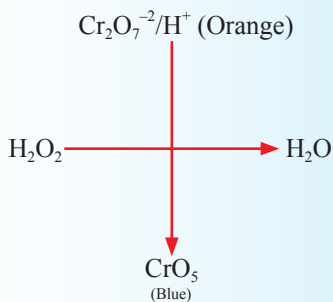


(i) **Chemical volcano:**

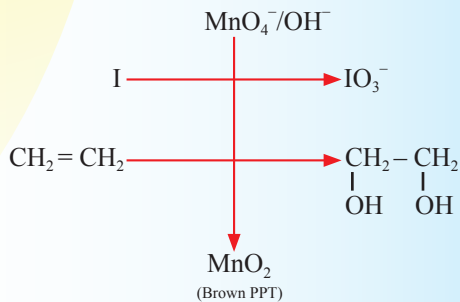
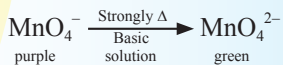
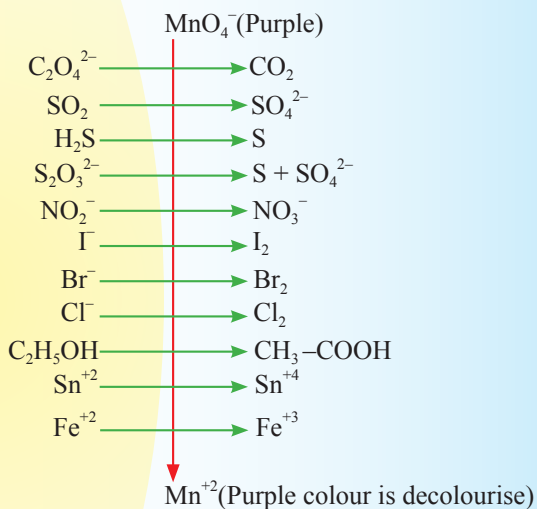


Reactions of $\text{Cr}_2\text{O}_7^{2-}$





Reaction of MnO_4^-



Coordination Chemistry

Addition compound

(two or more simple salt combining with fixed proportion of mass)

Double salt

* Lose their identity in aqueous solution

eg. $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ carnalite salt

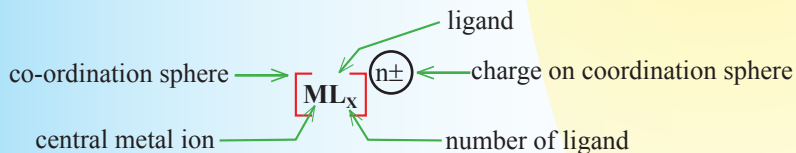
$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
potash alum

Co-ordination compound

* Retain their identity in aqueous solution

eg. $\text{K}_4[\text{Fe}(\text{CN})_6]$ Potassium hexacyanidoferrate (II)

REPRESENTATION OF COMPLEX COMPOUND



Co-ordination number = Number of electron pair accepted by central metal ion.

LIGAND

Chemical species which can donate electron pair.

Classification on the Basis of Denticity

(Denticity : –Number of electron pair donated by central metal atom or ion)

Monodentate (denticity = 1) :

eg. H^- , X^- , Py , N_2 , N^{3-} , N_2H_4 etc.

Bidentate (denticity = 2) :

eg. en, pn, bn, ox²⁻, acac⁻¹, gly⁻¹, dmg⁻¹

Polydentate (denticity = -2):

eg. dien, imda⁻², trien, nta³⁻, EDTA⁴⁻

Ambidentate : Ligand which have more than one donor site but at the time of donation only atom can donate electron pair.

eg. : (CN⁻, NC⁻), (NO₂⁻, ONO⁻), (SCN⁻, NCS⁻), (OCN⁻, NCO⁻), (S₂O₃²⁻, SO₂S²⁻)

Flexidentate ligand : Show more than one type of denticity.

eg. : CO₃²⁻, SO₄²⁻, CH₃COO⁻



Bidentate and Polydentate are also called chelating ligand.

Classification on the basis of electron donating and accepting tendency

Classical ligand : H₂O, NH₃ etc.

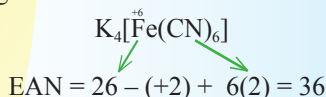
Non-classical ligand : CN⁻, NO⁺, NO, CO, PPh₃

π - donor ligand \Rightarrow C₂H₄, C₂H₂ etc.

BONDING IN COORDINATION COMPOUND

Effective atomic number & Sidgwick rule

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



- If EAN value is equal to atomic number of Noble gas then complex follow sidgwick rule of EAN.
- In carbonyl complex, if EAN value = Atomic number of Noble gas then carbonyl complex is more stable.

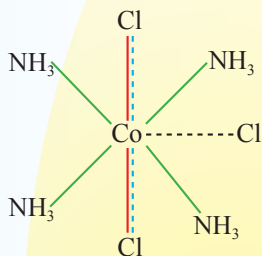
| | | |
|---------------------------|------------------------|------------------------|
| eg. [V(CO) ₆] | [Cr(CO) ₆] | [Mn(CO) ₆] |
| act as oxidising agent | stable complex | act as reducing agent |

- **Brown ring complex** **37**
Sodium nitroprusside 36
Zeise's Salt 84
Mn₂(CO)₁₀ 36
Fe₂(CO)₉ 36
Co₂(CO)₈ 36

WERNER'S CO-ORDINATION THEORY

- Metals possess two types of valencies PV & SV.
- PV is non-directional, represented by (dotted line) is satisfied by negative charge species.
- SV is directional, represented by _____ (solid line) and satisfied by negative or neutral species.
- Now a days primary valency and secondary valency is considered as oxidation & co-ordination number respectively.

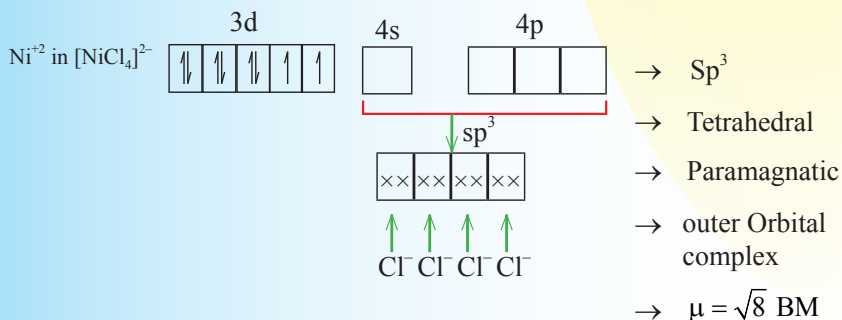
eg. $\text{CoCl}_3 \cdot 4\text{NH}_3$
 PV = 3, SV = 6
 C.N. = 6, Oxidation state = +3

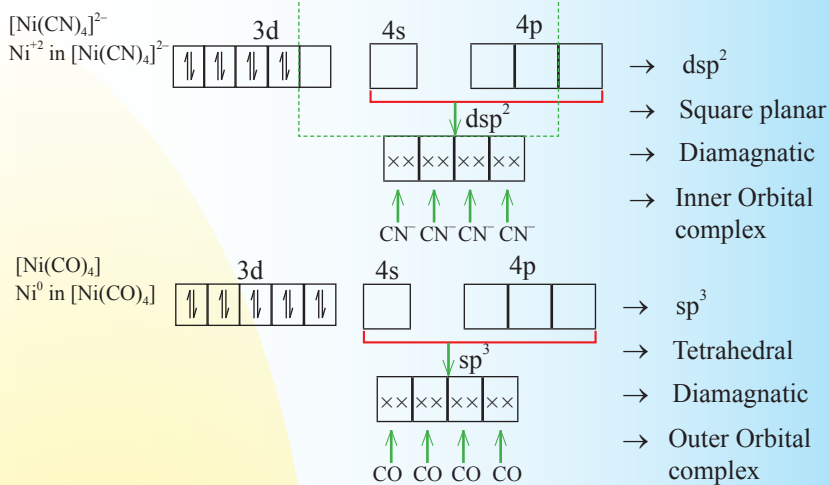


VBT

- Metal provides 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 pairs up the unpaired e^- of central metal atom where as weak field ligand does not.
- If unpaired e^- present in complex then complex is paramagnetic. If unpaired e^- is absent then diamagnetic.

eg. CN = 4 ; $[\text{NiCl}_4]^{2-}$

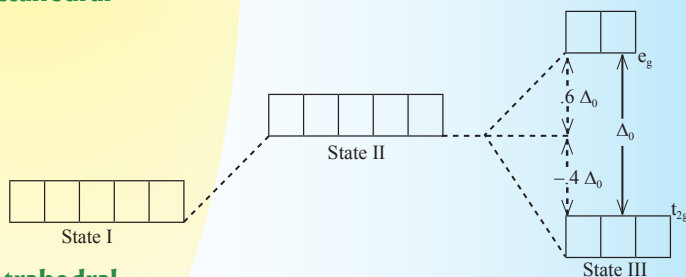




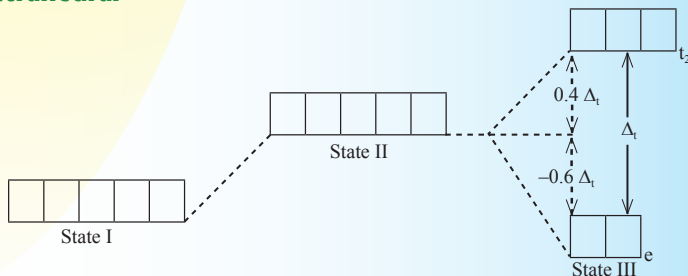
CRYSTAL FIELD THEORY

Crystal Field Theory : In the electric field of these negative charges, the five d-orbitals of the metal atom no longer have exactly same energy. Splitting of five degenerate d-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.

In octahedral



In tetrahedral



Orbitals which have same energy in a subshell are known as degenerate orbitals.

Series which shows the Relative Strength of Ligands

Γ^- (weakest) $< \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{edta}^{4-} < \text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$ (strongest)

Crystal Field Stabilisation Energy (CFSE)

(i) For octahedral CFSE = $[-0.4(n_{t_{2g}}) + 0.6(n_{e_g})] \Delta_0 + \text{Paring energy (P.E.)} \times x$

Where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

n_{e_g} = number of electron in e_g orbitals

x = number of electron pair

(ii) For tetrahedral CFSE

= $[-0.6(n_e) + 0.4(n_{t_2})] \Delta_t + \text{Paring energy (P.E.)} \times x$

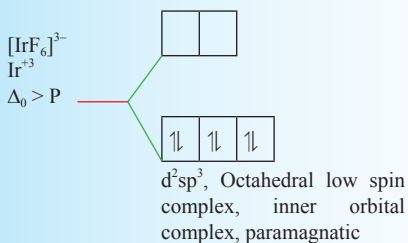
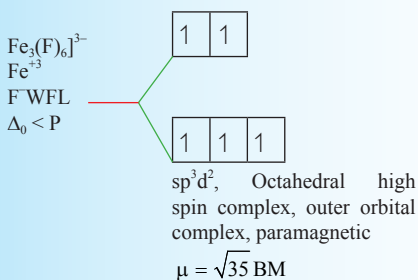
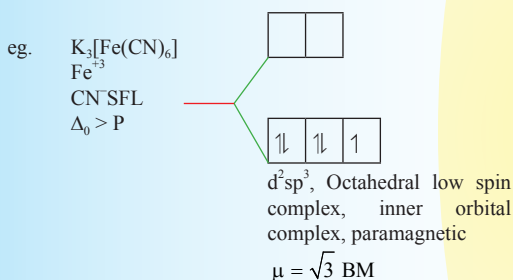
where n_{t_2} = number of electron in t_2 orbitals

n_e = number of electron in e orbitals

x = number of electron pair

\Rightarrow Follow Hund's Pauli & Aufbau rule.

CN-6

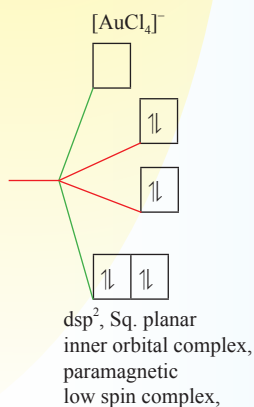
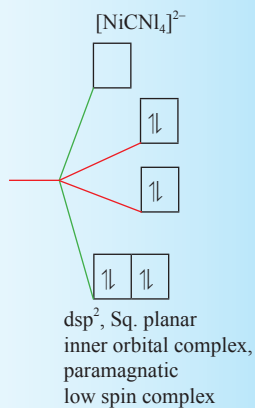
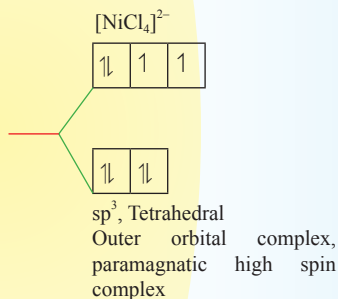


Exception

| | | |
|--|-----------|--------------|
| $[\text{Co}(\text{OX})_3]^{3-}$ | d^2sp^3 | diamagnetic |
| $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ | d^2sp^3 | diamagnetic |
| $[\text{NiF}_6]^{2-}$ | d^2sp^3 | diamagnetic |
| $[\text{Cr}(\text{NH}_3)_6]^{2+}$ | sp^3d^2 | paramagnetic |
| $[\text{Mn}(\text{NH}_3)_6]^{2+}$ | sp^3d^2 | paramagnetic |
| $[\text{Fe}(\text{NH}_3)_6]^{2+}$ | sp^3d^2 | paramagnetic |
| $[\text{CoL}_6]^{4+}$ (L = $\text{NO}_2^-/\text{CN}^-$) | d^2sp^3 | paramagnetic |

CN-4

eg.

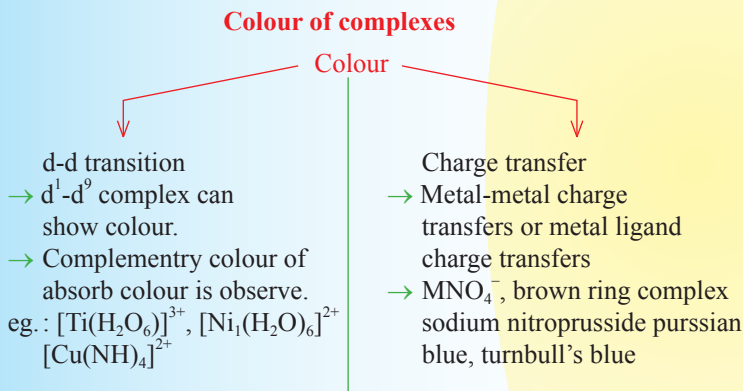


Exception

- d^3 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 CN^-4 with L
(where $L = NO_2^- / CN^- / NH_3$, etc.)

Factor affecting splitting

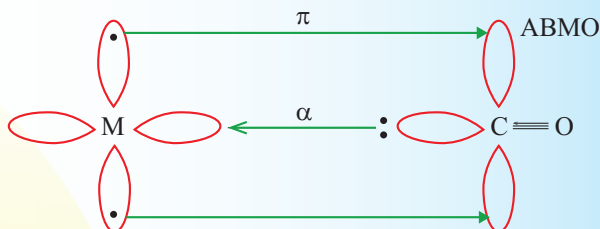
- Strength of ligand
- Oxidation state of central metal ion
- Transition series (d-series)
- Geometry (number of ligands)
- Chelation



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 nontransition 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 carbonyls compounds formed between metal and carbon monoxide belong to this class. $Ni(CO)_4$, $Fe(CO)_5$ etc.



IUPAC nomenclature of complex compounds

- For anionic complex (like $K_4[Fe(CN)_6]$)**
 Common name of normal cation (without numeral prefix) + name of ligands (with numeral prefix) + latin name of CMI along with suffix ate + oxidation state (in roman number).
 eg. : Potassium hexacyanoferrate (II)
- For cationic complex like $[Cu(NH_3)_4]SO_4$**
 Name of ligands (with numeral prefix) + Common name of CMI + oxidation state (In roman number) + Name of anion (without numeral prefix)
 eg. : Tetraammine copper (II) sulphate.
- For neutral complex (like $[Fe(CO)_5]$)**
 Name of ligands (with numeral prefix)
 + Common name of CMI + oxidation state (In roman number)
 eg. : Pentacarbonyl iron (0)
- Rule same just apply alphabetical order when write the name of ligands**
 e.g. $[Pt(NH_3)_2Cl_2]$
 Diamminedichloroplatinum (II)

STRUCTURAL ISOMERISM

- Ionisation isomerism** : Counter ion as a ligand & ligand act as counter ion.
 $[Co(H_2O)_5Cl]SO_4 \rightarrow [Co(H_2O)_5SO_4]Cl$
- Hydrate isomerism** : Number of water molecule inside & outside the co-ordinate sphere are different.
 $[Cr(H_2O)_6]Cl_3 \leftrightarrow [Cr(H_2O)_5Cl]Cl_2 \cdot H_2O \leftrightarrow [Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$
- Linkage** : Exhibit when ambidentate ligand is present in co-ordination sphere.
 $[NC \rightarrow Ag \leftarrow CN]^- \leftrightarrow [NC \rightarrow Ag \leftarrow NC]^- \leftrightarrow [CN \rightarrow Ag \leftarrow NC]^-$
- Co-ordination isomerism** : Exhibit when both are cationic & anionic complex
 $[Pt(NH_3)_4] [PtCl_4] \leftrightarrow [Pt(NH_3)_3Cl] [Pt(NH_3)Cl_3]$

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 coordinated ligand having chiral center.
- Square planar complex
 $[Ma_2b_2]^{n\pm}$, $[Ma_2bc]^{n\pm}$, $[Mabcd]^{n\pm}$, $[M(AB)cd]^{n\pm}$
 $[M(AB)(CD)]^{n\pm}$ show geometrical isomerism
- $[Mabcd]^{n\pm}$ form two cis and one trans.
- 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.

| CN-6 | | | |
|---|-------------------------|----------------------|----------------|
| Number of Possible Isomers for Specific Complexes | | | |
| Formula | Number of stereoisomers | Pairs of Enantiomers | Number of G.I. |
| Ma_4b_2 | 2 | 0 | 2 |
| Ma_3b_3 | 2 | 0 | 2 |
| Ma_4bc | 2 | 0 | 2 |
| Ma_3b_2c | 3 | 0 | 3 |
| Ma_3bcd | 5 | 1 | 4 |
| $Ma_2b_2c_2$ | 6 | 1 | 5 |
| Ma_2b_2cd | 8 | 2 | 6 |
| Ma_2bcde | 15 | 6 | 9 |
| $Mabcdef$ | 30 | 15 | 15 |
| $M(AA)(BC)de$ | 10 | 5 | 5 |
| $M(AB)(AB)cd$ | 11 | 5 | 6 |
| $M(AB)(CD)ef$ | 20 | 10 | 10 |
| $M(AB)_3$ | 4 | 2 | 2 |



Uppercase letter represent chelating ligands and lowercase letter represent monodentate ligands.

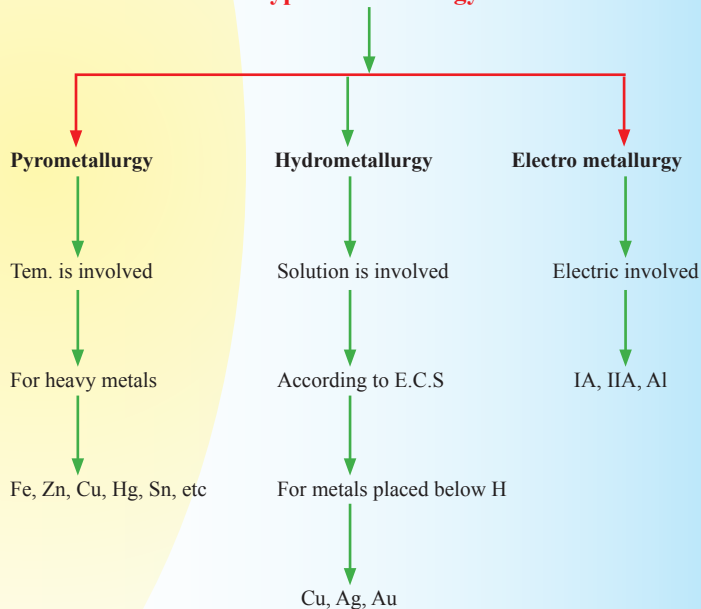


Metallurgy

Bunch of Process to Extract Metal from their Respective Ore

Ore : Minerals from which metal can be extracted economically :

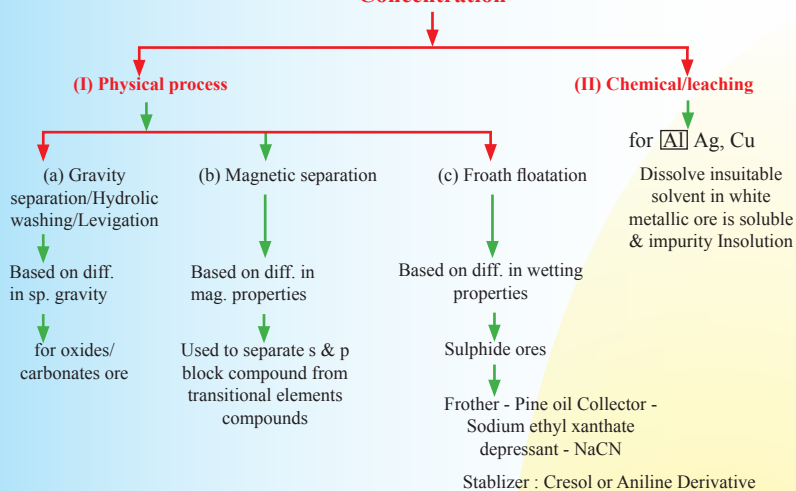
Types of metallurgy



Metallurgical process :

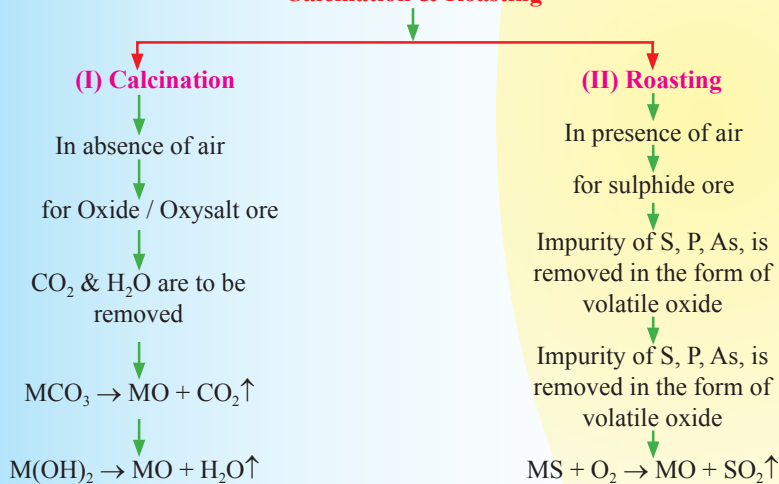
- 1. Mining :** Ore obtain in big lumps (less reactive)
- 2. Crushing/grinding/pulverization :** big lumps convert into powder (more reactive)
- 3. Concentration :** To remove matrix/gangue from ore
To increase the concentration of ore particle in ore sample.

Concentration



Ag, Au, are concentrated by cyanide process.

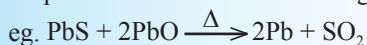
Calcination & Roasting



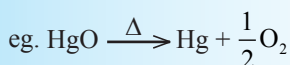
Reduction : To obtain metal (95 to 98%) from metal oxide.

Self reduction

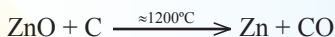
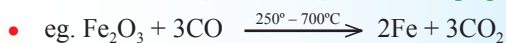
- Sulphide ore itself act as reducing agent.



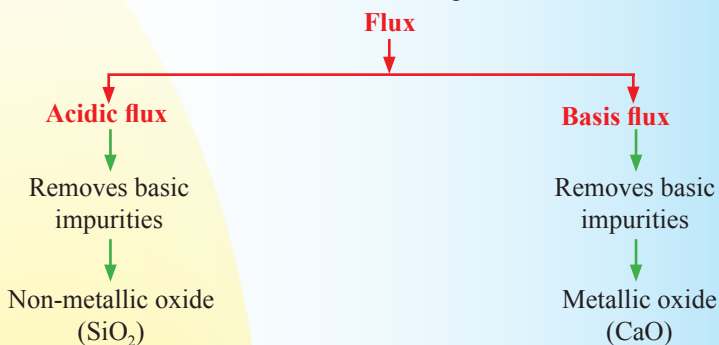
- Thermal decomposition



Carbon reduction (Smelting) : Reducing agent C/CO



Flux - substance to convert non-fusible impurities to fusible one.

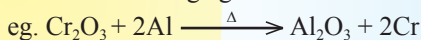


Imp. point – Above 710°C is reducing agent.

– Below 710°C CO is better reducing agent.

Aluminum reduction method : (Thermite process)

- Al act as reducing agent



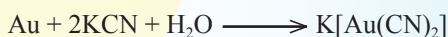
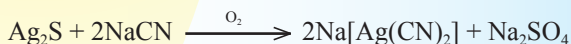
Thermite mixture mass ratio : $\text{Cr}_2\text{O}_3 : \text{Al} = 3 : 1$

METAL DISPLACEMENT REDUCTION

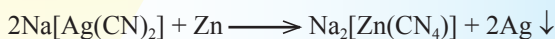
- Metal placed below H. in E.C.S.
- Ag, Au, Cu

Example of extraction of

(i) Cyanidation (Leaching Process)



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



ELECTROLYTIC REDUCTION

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

Example :-

(i) Extraction of Al(Hall-Herault)

– Al can be extracted from Al_2O_3

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

– $Na_3 AlF_6$ & CaF_2 increase the conductivity & reduce the fusion temp.

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

(iii) Extraction of Na (Down cell process)

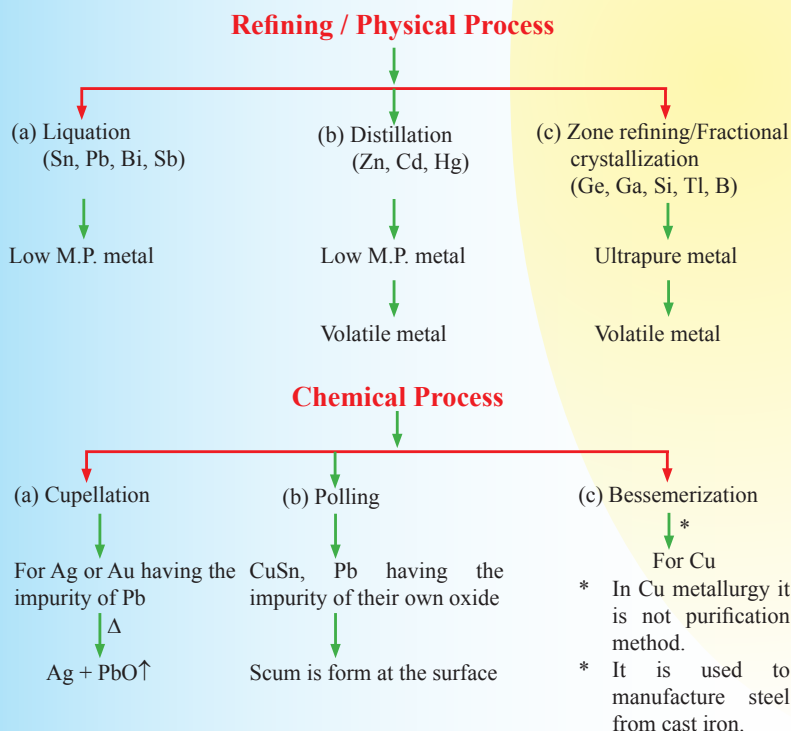
– Na can be extracted from NaCl

– Down Process Neutral flux ($CaCl_2$) 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%)



Thermal decomposition (Vapour Phase Refining)

(a) Van arkel de Boer
(Ti, Zr, Hf, B, Th)

Impure metal \downarrow Pure metal



Volatile ^{Pure}

Impurity + I₂ \rightarrow No reaction
(Or not form volatile product)

(a) Mond's process
(for Ni)



Impurity + CO \rightarrow X

(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 deposited at cathod.

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 temperatue. Gibbs energy of reaction must be negative.
- At high temperature 'C' is the best reducing agent.
- At low temperature 'CO' is the best redusing agent.
- In blast fornace reduction takes plae 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 | Reffining | Remarks |
|-------------------------|--|---|--|--|
| Aluminium E° = -1.66 | 1. Bauxite, Al ₂ O ₃ .xH ₂ O 2. Cryolite, Na ₃ AlF ₆ | Electrolysis of Al ₂ O ₃ dissolved in molten Na ₃ AlF ₆ + CaF ₂ | Electrolytic refining by Hoop's cell | For the extraction, a good source of electricity is required |

| Metal | Occurrence | Common method of extraction | Refining | Remarks |
|-----------------------------|--|--|--|--|
| Iron $E^\circ = -0.44$ | 1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4 3. Limonite, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ 4. Siderite, FeCO_3 | Reduction of the oxide with CO and coke in Blast furnace | Bessemerization (impurities has more affinity for O_2 as compare to Fe) | Temperature approaching 2170K is required |
| Copper $E^\circ = -0.34$ | 1. Copper pyrites, CuFeS_2 2. Copper glance, Cu_2S 3. Malachite, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ 4. Cuprite, Cu_2O 5. Azurite, $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ | Roasting of sulphide partially and reduction | (i) Polling (ii) Electrolytic method | It is self reduction in a specially designed converted. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores. |
| Zinc $E^\circ = -0.76$ | 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 purified by fractional distillation | For ZnO , carbon is better reducing agent than CO and Zn is obtain in vapours form $\text{ZnO} + \text{C} \xrightarrow{\text{high T}} \text{Zn} + \text{CO}$ |
| Mg $E^\circ = -2.36$ | 1. Carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 2. Magnesite, MgCO_3 | Electrolysis of fused MgCl_2 with KCl | | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is heated in the excess current of dry HCl gas to produce anhydrous MgCl_2 |
| Sn $E^\circ = -0.14$ | 1. Cassiterite, SnO_2 (Tin stone) | Reduction of the SnO_2 with carbon. $\text{SnO}_2 + 2\text{C} \rightarrow \text{Sn} + 2\text{CO}$ | Polling and Liquidation | Ore contain impurity of wolframite, $\text{FeWO}_4 + \text{MnWO}_4$ (magnetic separation) |

| Metal | Occurrence | Common method of extraction | Refining | Remarks |
|-------------------------|---|---|------------------------------------|---|
| Pb $E^\circ = -0.13$ | 1. Galena, Pbs | Roasting, then self reduction or Reduction of PbO (Roasted ore) with carbon $PbS + 2PbO \rightarrow 3Pb + SO_2$ $PbO + C \rightarrow Pb + CO$ | Liquadation & electrolytic method. | |
| Ag $E^\circ = 0.80$ | 1. Argentite- Ag ₂ S, native Silver | Hydro metallurgy $Ag_2S + 4NaCN + N_2S \rightarrow 2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Ag$ | Cupelation & electrolytic method | In hydro mettallurgy Ag obtain in the form of dark amorphous ppt. |
| Au $E^\circ = 1.40$ | Native ore | 1. Amalgamation. 2. Cynide process | Cupelation & electrolysis method. | In hydro mettallurgy Au obtain in the form of dark amorphous ppt. |

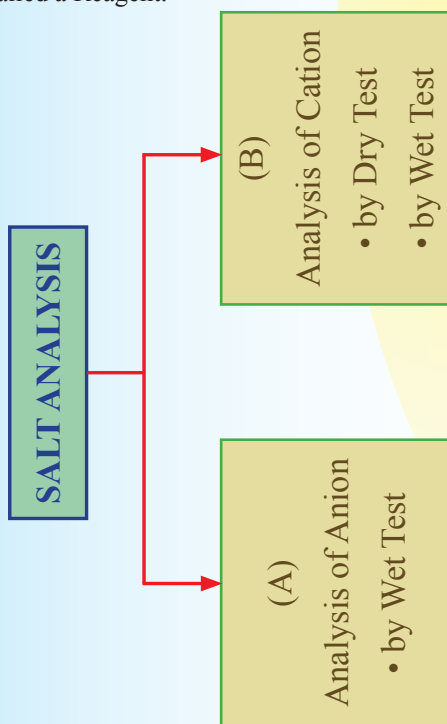


Salt Analysis

DEFINITION

The branch of chemical analysis which aims to find out the constituents of a mixture of compound is known as Qualitative Analysis.

The Identification of a substances usually involves its conversion into a new substance possessing characteristic properties with the help of one or more substance of known composition. The Substance which is used to bring about such change is called a Reagent.



ANALYSIS OF ACIDIC RADICAL

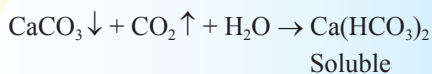
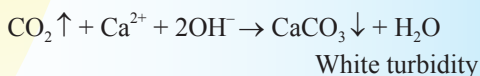
Classification of Acidic Radical

| Class - A (Form volatile product with acid) | Class - B (Does not form volatile product with acid) |
|---|--|
| Sub group-I | Sub group-I |
| (Form volatile product with dil. HCl/ dil. H ₂ SO ₄) CO ₃ ²⁻ , HCO ₃ ⁻ , SO ₃ ²⁻ , HSO ₃ ⁻ , S ₂ O ₃ ²⁻ , S ²⁻ , CH ₃ COO ⁻ , NO ₂ ²⁻ | (Detected by precipitation reaction) SO ₄ ²⁻ , PO ₄ ³⁻ , AsO ₃ ³⁻ , AsO ₄ ³⁻ |
| Sub group-II | Sub group-II |
| (Form volatile product with conc. H ₂ SO ₄) F ⁻ , Cl ⁻ , Br ⁻ , I ⁻ , NO ₃ ⁻ , BO ₃ ³⁻ , C ₂ O ₄ ²⁻ + sub group-I | (Detected by redox reaction) CrO ₄ ²⁻ , Cr ₂ O ₇ ²⁻ , MnO ₄ ⁻ , MnO ₄ ⁻² |

- CO₂ is colourless, odourless gas evolved with brisk effevescence, Detected by lime water test.
- So₂ is colourless, Suffocating gas with burning sulphur odour. Detected by lime water test or by passing in Cr₂O₇²⁻/H⁺ solution.
- H₂S is a colourless gas having rotten egg odour.
- CH₃COOH has colourless fumes having vinegar odour.
- NO₂/Br₂ is brown gas.
- I₂ is violet gas.

LIME WATER / BARYTA WATER TEST

When CO₂ is passed in lime water or baryta water then white turbidity (milky appearance) is formed due to the formation of soluble carbonate but when excess of CO₂ is passed then white turbidity disappeared due to formation of soluble bicarbonate.



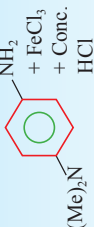
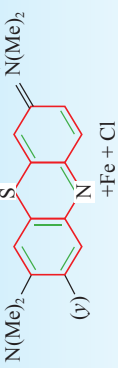
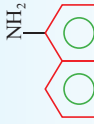
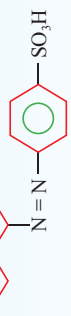
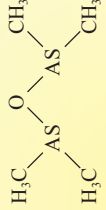
SO₂ also gives similar observation.


ACIDIC RADICAL TABLE

| | dil. H_2SO_4 | Conc. H_2SO_4 | $CaCl_2$ | $BaCl_2$ | $HgCl_2$ | $AgNO_3$ | $Pb(OAc)_2$ | MnO_4^-/H^+ |
|--------------------|--------------------------------|--------------------------------|------------------------------|--------------------------------|---|----------------------------------|-------------------------------------|----------------------------|
| CO_3^{2-} | $CO_2 \uparrow$ | $CO_2 \uparrow$ | $CaCO_3 \downarrow$ white | $BaCO_3 \downarrow$ white | $HgCO_3 \cdot 3HgO \downarrow$ Reddish brown | $Ag_2CO_3 \downarrow$ | $PbCO_3 \cdot 2Pb(OH)_2 \downarrow$ | – |
| $HCO_3^- + \Delta$ | $CO_2 \uparrow$ | $CO_2 \uparrow$ | $CaCO_3 \downarrow$ | $BaCO_3 \downarrow$ | $HgCO_3 \cdot 3HgO \downarrow$ Reddish brown | $Ag_2CO_3 \downarrow$ | $PbCO_3 \cdot 2Pb(OH)_2 \downarrow$ | – |
| SO_3^{2-} | $SO_2 \uparrow$ | $SO_2 \uparrow$ | $CaSO_3 \downarrow$ white | $BaSO_3 \downarrow$ white | – | $Ag_2SO_3 \downarrow$ white | $PbSO_3 \downarrow$ white | SO_4^{2-} |
| $S_2O_3^{2-}$ | $SO_2 \uparrow + S \downarrow$ | $SO_2 \uparrow$ | – | $BaS_2O_3 \downarrow$ white | $HgS_2O_2 \downarrow$ white | $Ag_2S_2O_3 \downarrow$ white | $PbS_2O_3 \downarrow$ white | $SO_4^{2-} + S \downarrow$ |
| S^{2-} | $H_2S \uparrow$ | $S \downarrow + SO_2 \uparrow$ | – | $BaS \downarrow$ black | $HgS \downarrow$ black | $Ag_2S \downarrow$ black | $PbS \downarrow$ black | $S \downarrow$ |
| NO_2^- | $NO_2 \uparrow$ | $NO_2 \uparrow$ | – | – | – | $AgNO_2 \downarrow$ | – | NO_3^- |
| CH_3COO^- | $CH_3COOH \uparrow$ | $CH_3COOH + SO_2 \uparrow$ | – | – | – | – | – | – |
| I^- | | $I_2 \uparrow$ violet | – | – | $HgI_2 \downarrow$ scarlet red | $AgI \downarrow$ yellow | $PbCl_2 \downarrow$ dark yellow | $I_2 \uparrow$ |

| | dil. H_2SO_4 | Conc. H_2SO_4 | CaCl_2 | BaCl_2 | HgCl_2 | AgNO_3 | Pb(OAc)_2 | $\text{MnO}_4^-/\text{H}^+$ |
|-----------------------------|------------------------------|---|---|---|---|--|--------------------------------------|-----------------------------|
| Cl^- | | $\text{HCl}\uparrow$ | – | – | – | $\text{AgCl}\downarrow$ white | $\text{PbCl}_2\downarrow$ white | $\text{Cl}_2\uparrow$ |
| Br^- | | $\text{Br}_2\uparrow$ brown | – | – | – | $\text{AgBr}\downarrow$ pale yellow | $\text{PbBr}_2\downarrow$ white | $\text{Br}_2\uparrow$ |
| $\text{C}_2\text{O}_4^{2-}$ | – | $\text{CO}_2\uparrow + \text{CO}\uparrow$ | $\text{CaC}_2\text{O}_4\downarrow$ white | $\text{BaC}_2\text{O}_4\downarrow$ white | – | $\text{Ag}_2\text{C}_2\text{O}_4\downarrow$ white | – | $\text{CO}_2\uparrow$ |
| BO_2^- | – | $\text{H}_3\text{BO}_3\uparrow$ | $\text{Ca(BO}_2)_2\downarrow$ white | $\text{Ba(BO}_2)_2\downarrow$ white | – | $\text{AgBO}_2\downarrow$ white | – | – |
| NO_3^- | – | $\text{NO}_2\uparrow$ | – | – | – | – | – | – |
| SO_4^{2-} | – | – | $\text{CaSO}_4\downarrow$ white | $\text{BaSO}_4\downarrow$ curdy white ppt | $\text{HgSO}_4 \cdot 2\text{HgO}\downarrow$ yellow | – | $\text{PbSO}_4\downarrow$ white | – |
| PO_4^{3-} | – | – | $\text{CaHPO}_4\downarrow$ white | $\text{BaHPO}_4\downarrow$ white | – | $\text{Ag}_3\text{PO}_4\downarrow$ yellow | – | – |
| CrO_4^{2-} | – | – | – | $\text{BaCrO}_4\downarrow$ yellow | – | $\text{Ag}_2\text{CrO}_4\downarrow$ brick red | $\text{PbCrO}_4\downarrow$ yellow | – |

SPECIFIC REACTION OF ACIDIC RADICAL

| Anion | Reaction Name /with | Reagent | Product | Observation |
|-------------|---------------------------|---|--|---|
| S^{2-} | Sodium Nitro Prusside | $Na_2[Fe(CN)_5NO]$ | $Na_4[Fe(CN)_5NOS]$ | Purple Complex |
| S^{2-} | Methylene blue Test |  $(Me)_2N$ $+ FeCl_3$ $+ Conc.$ HCl |  $+ Fe + Cl$ | Methylene Blue |
| NO_2^- | Gries Illosavay Test | (i) Sulphanilic acid (ii) 1, Methyl Amine |  $N = N$  SO_3H | Red Azo dye |
| NO_2^- | Brown Ring Test | $FeSO_4 + dil. H_2SO_4$ | $[Fe(H_2O)_5NO]SO_4$ | Brown Ring |
| CH_3COO^- | Cacodyl Test | As_2O_3 |  CH_3 CH_3 | Nauseating odour |
| CH_3COO^- | $FeCl_3$ Sol ⁿ | $FeCl_3 + H_2O \xrightarrow{boil}$ | $[Fe_3(HO)_2(CH_3OO)_6]^+$ | Blood Red solution ↓ Boiling Reddish Brown ppt. |

| Anion | Reaction Nmae /with | Reagent | Product | Observation |
|--|--|--|--|--|
| NO_3^- | Brown Ring test | $\text{FeSO}_4 + \text{Conc. H}_2\text{SO}_4$ | $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ | Brown Ring |
| $\text{C}_2\text{O}_4^{2-}$ | $\text{Mn}^{+2} + \text{NaOH}$ | $\text{NaOH} + \text{Mn}^{+2} \xrightarrow{\Delta}$ | $[\text{Mn}(\text{C}_2\text{O}_4)_3]^{3-}$ | Red Complex |
| Br^- | Layer Test | Cl_2 Water + CCl_4 | $\text{Br}_2 + \text{CCl}_4$ | Red layer |
| I^- | Layer Test | Cl_2 Water + CCl_4 | $\text{I}_2 + \text{CCl}_4$ | Violet Layer |
| I^- | HgCl_2 | HgCl_2 | HgI_2 | Red/yellow |
| Cl^- | Chromyl Chloride Test | (i) $\text{K}_2\text{Cr}_2\text{O}_7(\text{s}) + \text{conc. H}_2\text{SO}_4$ (ii) NaOH (iii) $\text{Pb}(\text{CH}_3\text{COO})_2 + \text{CH}_3\text{COOH}$ | CrO_2Cl_2 CrO_4^{2-} \downarrow PbCrO_4 | Reddish brown Vapour \downarrow Yellow Solution \downarrow Yellow ppt. |
| BO_3^{3-} | Green Flame Test | $\text{Conc. H}_2\text{SO}_4 + \text{ROH} + \Delta$ (Flame) | $\text{B}(\text{OR})_3$ | Green edge flame |
| BO_3^{3-} | Modified Green Flame Test | $\text{CaF}_2 + \text{Conc. H}_2\text{SO}_4$ | $\text{BF}_3 \uparrow + \text{Ca}(\text{HSO}_4)_2 + \Delta$ | Green flame |
| PO_4^{3-} | Ammonium molybdate | $(\text{NH}_4)_2\text{MoO}_4 + \text{dil HNO}_3 + 30 - 40^\circ \text{C}$ | $\text{Na}_3\text{MoO}_4 \cdot 12\text{MoO}_3$ | Canary yellow ppt. |
| CrO_4^{2-} / Cr_2O_7 | Acidic Solution of H_2O_2 + pyridine | $\text{H}_2\text{O}_2 + \text{H}^+$ +  | CrO_5 | Blue Solution |

BASIC RADICAL ANALYSIS

Dry Text of Cation

Flame test : used for s-block cation (except Be^{+2} , Mg^{+2})

| | | | | | | | |
|-----------------------------|---------------|-----------------|--------------|------------------|------------------|------------------|------------------|
| Cation: | Li^+ | Na^+ | K^+ | Ca^{+2} | Sr^{+2} | Ba^{+2} | Cu^{+2} |
| Observation: (Naked eye) | Carmine red | Golden yellow | Lilac | Brick Red | Crimosn Red | Apple green | Green flame |
| Cobalt glass: | | flame disappear | crimson red | Green | Purple | Bluish green | Green flame |

Borax Bead Text

- Used for cloured cation (d-block cation)
- Given salt heated on borax bead than metal metaborate are form.
- Metal metaborate on heating show characteristic bead colour.

| | Oxidizing flame | | Reducing flame | |
|----|-----------------|----------|----------------|------------|
| | Hot | Cold | Hot | Cold |
| Mn | Violet | Amethyst | Colourless | Colourless |
| Cr | Yellow | Yellow | Green | Green |
| Fe | Yellowish brown | Green | Green | Green |
| Co | Blue | Blue | Blue | Blue |
| Ni | Violet | Brown | Grey | Grey |
| Cu | Green | Blue | Colourless | Opaque red |

Charcoal Cavity Text

Heat salt with Na_2CO_3 in charcoal cavity

Zn^{+2} In hot yellow and in cold white residue.

Pb^{+2} Yellow residue in hot and grey metal in cold.

As^{+3} White residue with garlic odour.

Cd^{+2} Brown residue.

If white residue is obtain then add. $\text{Co}(\text{No}_3)_2$ and heat.

| | | |
|------------------|-------------------------------|-----------------|
| Zn^{+2} | $\text{ZnO} \cdot \text{CoO}$ | Rinmann's Green |
| Al^{+3} | Al_2O_3 | Thenard Blue |
| Mg^{+2} | $\text{MgO} \cdot \text{CoO}$ | Pink residue |
| Sn^{+2} | $\text{SnO} \cdot \text{CoO}$ | Bluish residue |

CLASSIFICATION OF BASIC RADICAL

| Group | Basic Radical | Reagent used | Precipitate form |
|-----------|---|---|--|
| Group-I | $\text{Pb}^{+2}, \text{Hg}_2^{+2}$ | dil HCl | AgCl PbCl_2 Hg_2Cl_2 white ppt. |
| Group-II | $\text{Cu}^{+2}, \text{Pb}^{+2}, \text{Hg}^{+2},$ $\text{Cd}^{+2}, \text{Bi}^{+3}$ | $\text{H}_2\text{S} + \text{dil. HCl}$ | $\text{Cu}_2\text{S}, \text{PbS}, \text{HgS}, \text{CdS}, \text{Bi}_2\text{S}_3$ Black yellow black |
| | $\text{Sn}^{+2}, \text{Sn}^{+4}, \text{As}^{+3},$ $\text{As}^{+5}, \text{Sb}^{+3}, \text{Sb}^{+5}$ | | SnS SnS_2 $\text{As}_2\text{S}_3, \text{As}_2\text{S}_5$ $\text{Sb}_2\text{S}_3, \text{Sb}_2\text{S}_5$ Brown Brown yellow Gray |
| Group-III | $\text{Cr}^{+3}, \text{Al}^{+3}, \text{Fe}^{+3}$ | $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ | $\text{Al}(\text{OH})_3$ $\text{Fe}(\text{OH})_3$ $\text{Cr}(\text{OH})_3$ gelatinous reddish green white brown |
| Group-IV | $\text{Zn}^{+2}, \text{Mn}^{+2}, \text{Ni}^{+2},$ Co^{+2} | $\text{H}_2\text{S} + \text{NH}_4\text{OH}$ | ZnS MnS NiS CoS white buff black |
| Group-V | $\text{Ca}^{+2}, \text{Sr}^{+2}, \text{Ba}^{+2}$ | $(\text{NH}_4)_2\text{CO}_3 + \text{NH}_4\text{OH}$ | $\text{CaCO}_3, \text{SrCO}_3, \text{BaCO}_3$ white |

TEST OF BASIC RADICAL

| | Ag ⁺ | Hg ₂ ²⁺ | Pb ²⁺ | Cu ²⁺ | Hg ²⁺ | Cd ²⁺ | Al ³⁺ |
|---------|-------------------------------------|---|---|--|---|--------------------------------------|--|
| KI | AgI Yellow | Hg ₂ I ₂ Green | PbI ₂ Yellow | CuI + I ₃ ⁻ White solution | Hg ₂ I ₂ Scarlet Red | — | — |
| ex KI | — | Hg + [HgI ₄] ²⁻ Black | [PbI ₄] ²⁻ soluble complex | — | [HgI ₄] ²⁻ Red solution | — | — |
| KCN | AgCN White | Hg + Hg(CN) ₂ | Pb(CN) ₂ white | CuCN + [CN] ₂ ↑ | — | Cd(CN) ₂ White | — |
| ex KCN | [Ag(CN) ₂] ⁻ | — | — | K ₃ [Cu(CN) ₄] soluble complex | — | [Cd(CN) ₄] ²⁻ | — |
| NaOH | Ag ₂ O Brown | Hg ₂ O Black | Pb(OH) ₂ White | Cu(OH) ₂ Pale Blue | HgO yellow | Cd(OH) ₂ White | Al(OH) ₃ Gelatinous white |
| ex NaOH | — | — | Na ₂ [Pb(OH) ₄] soluble complex | — | — | — | Na[Al(OH) ₄] soluble complex |

| | Ag^+ | Hg_2^{2+} | Pb^{2+} | Cu^{2+} | Hg^{2+} | Cd^{2+} | Al^{3+} |
|--|--|--|-----------------------------------|--|---|----------------------------|--|
| NH_4OH | Ag_2O Brown | $\text{Hg} + \text{HgO}$, HgNH_2NO_3 | Pb(OH)_2 White | Cu(OH)_2 Pale Blue | HgO , HgNH_2Cl White | Cd(OH)_2 White | Al(OH)_3 Gelatinous white |
| ex NH_4OH | $[\text{Ag(NH}_3)_2]^+$ | — | — | $[\text{Cu(NH}_3)_4]^{2+}$ Deep blue | — | $[\text{Cd(NH}_3)_4]^{2+}$ | — |
| $\text{H}_2\text{S}^*/(\text{NH}_4)_2\text{S}$ | Ag_2S Black | $\text{Hg} + \text{HgS}$ black | PbS Black | CuS Black | HgS Black | CdS Yellow | Al(OH)_3 Gelatinous white |
| K_2CrO_4 | Ag_2CrO_4 Red | Hg_2CrO_4 Red | PbCrO_4 Yellow | — | — | — | — |
| $\text{Na}_2\text{S}_2\text{O}_3$ | $\text{Ag}_2\text{S}_2\text{O}_3$ White | — | PbS_2O_3 White | $\text{Cu}_2\text{S}_2\text{O}_3$ White | HgS_2O_3 white | — | — |
| $\text{K}_4[\text{Fe(CN)}_6]$ | $\text{Ag}_3[\text{Fe(CN)}_6]$ White | — | — | $\text{Cu}_2[\text{Fe(CN)}_6]$ Brown | — | — | — |
| $\text{K}_3[\text{Fe(CN)}_6]$ | — | — | — | $\text{Cu}_3[\text{Fe(CN)}_6]$ Green | — | — | — |

TEST OF BASIC RADICAL

| | Cr ⁺³ | Fe ⁺³ | Fe ⁺² | Zn ⁺² | Mn ⁺² | Ni ⁺² | Co ⁺² |
|--------------------|-------------------------------------|--|--|--|---|--|--|
| KI | — | Fe ₂ + I ₂ yellowish brown sol. | — | — | — | — | — |
| ex KI | — | — | — | Zn(CN) ₂ White | — | — | — |
| KCN | — | Fe(CN) ₃ Brown | Fe(CN) ₂ yellowish brown | — | Mn(CN) ₂ , Mn(OH) ₂ Pink | Ni(CN) ₂ green | Co(CN) ₂ Reddish Brown |
| ex KCN | — | K ₄ [Fe(CN) ₆] Yellow | K ₄ [Fe(CN) ₆] Pale yellow | — | — | K ₂ [Ni(CN) ₄] Soluble Complex | [Co(CN) ₆] ⁻¹ Brown Solution |
| NaOH | Cr(OH) ₃ Green | Fe(OH) ₃ Reddish Brown ppt | Fe(OH) ₂ Dirty Green | Zn(OH) ₂ White | Mn(OH) ₂ Pink | Ni(OH) ₂ Green | Co(OH)Cl Blue |
| ex NaOH | Na[[Al(OH) ₄] Yellow | — | — | Na ₂ [Zn(OH) ₄] | — | — | (CoOH) ₂ pink |
| NH ₄ OH | Cr(OH) ₃ Green | Fe(OH) ₃ Reddish Brown ppt | Fe(OH) ₂ Dirty Green | Zn(OH) ₂ | — | Ni(OH) ₂ Green | Co(OH)Cl |

| | Cr ⁺³ | Fe ⁺³ | Fe ⁺² | Zn ⁺² | Mn ⁺² | Ni ⁺² | Co ⁺² |
|--|---|---|---|--|---|---|--|
| ex NH ₄ OH | [Cr(NH ₃) ₆] ³⁺ Pink/violet | — | — | [Zn(NH ₃) ₄] ²⁺ | — | Ni[(NH ₃) ₆] ²⁺ Deep blue | [Co(NH ₃) ₆] ²⁺ Yellow |
| H ₂ S/(NH ₄) ₂ S | Cr(OH) ₃ Green | FeS + S Black yellow | FeS Black | ZnS White | MnS Pink | NiS Black | CoS Black |
| K ₂ CrO ₄ | — | — | — | — | — | — | — |
| Na ₂ S ₂ O ₃ | — | Fe ⁺² Green solution | — | — | — | — | — |
| K ₄ [Fe(CN) ₆] | — | Fe ₄ [Fe(CN ₆) ₃ Prussian blue | K ₃ Fe[Fe(CN) ₆] | K ₂ Zn ₃ [Fe(CN) ₆] White | Mn ₂ [Fe(CN) ₆] White | Ni ₂ [Fe(CN) ₆] Light green | Co ₂ [Fe(CN) ₆] Green |
| K ₃ [Fe(CN) ₆] | — | Fe[Fe(CN ₆)] Brown | Fe ₃ [Fe(CN ₆) ₂ Turnbull's blue | — | — | — | — |

OTHER IMPORTANT REACTION OF BASIC RADICAL

| Basic radical | Reagent | Product | Observation |
|------------------|------------------------------|--|-----------------------|
| Fe^{+3} | SCN^- | $\text{Fe}(\text{SCN})_3$ | Blood red colouration |
| Ni^{+2} | $\text{dmg} / \text{NH}_4^+$ | $[\text{Ni}(\text{dmg})_2]$ | Rosy red complex |
| Co^{+2} | KNO_2 | $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ | Yellow ppt |
| Hg^{+2} | $\text{SnCl}_2(\text{ex})$ | Hg | Grey / black |
| K^+ | HClO_4 | KClO_4 | White ppt |

