CHAPTER

1

Some Basic Concepts of Chemistry

SOME USEFUL CONVERSION FACTORS

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

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

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

$$1\ \text{atm} = 760\ \text{mm or torr}$$

$$= 101325\ \text{Pa or Nm}^{-2}$$

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

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

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

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

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

ATOMIC MASS OR MOLECULAR MASS

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

$C \rightarrow 12$ amu

$NH_3 \rightarrow 17$ amu

Actual Mass

Mass of one atom or molecule in grams

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

$CH_4 \rightarrow 16 \times 1.6 \times 10^{-24}$ g

Relative Atomic Mass or Relative Molecular Mass

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

$C \rightarrow 12$

$CH_4 \rightarrow 16$

It is unitless

GRAM ATOMIC MASS OR GRAM MOLECULAR MASS

Mass of one mole of atom or molecule

$$C \rightarrow 12\ g$$

$$CO_2 \rightarrow 44\ g$$

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 [$N_A = 6.022 \times 10^{23}$]

$$1u = 1amu = (1/12)^{th} \text{ of mass of 1 atom of } C^{12} = \frac{1g}{N_A}$$

$$= 1.66 \times 10^{-24}\ g$$

For Elements

- 1 g atom = 1 mole of atoms = N_A atoms
- g atomic mass (GAM) = mass of N_A atoms in g
- Mole of atoms = $\frac{\text{Mass }(g)}{\text{GAM or molar mass}}$

For Molecule

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

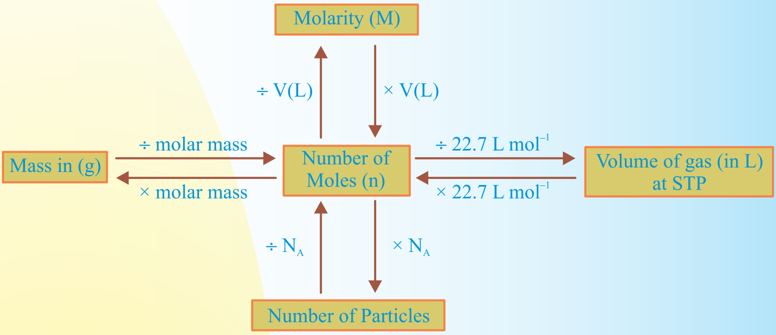
For Ionic Compounds

- 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.
- 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

$$aA + bB \longrightarrow cC + dD$$

- 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 stoichiometic amount of components may be related as

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

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 × 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 × ***specific heat capacity*** **(*cal/gm-°C*) ≈ 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	$X_A = \dfrac{\text{Mole of A}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \ldots}$ $X_B = \dfrac{\text{Mole of B}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \ldots}$	Ratio of number of moles of one component to the total number of moles.
Molarity	$M = \dfrac{\text{Mole of solute}}{\text{Volume of solution (in L)}}$	Moles of solute in one liter of solution.
Molality	$m = \dfrac{\text{Mole of solute}}{\text{Mass of solvent (Kg)}}$	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:

$$\text{Final molarity} = \frac{\text{Total moles}}{\text{Total volume}} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

(ii) Dilution Effect: Final molarity, $M_2 = \dfrac{M_1V_1}{V_1 + V_2}$

Volume Strenght of H_2O_2 Solutions

Labelled as 'volume H_2O_2' means volume of O_2 (in litre) at 1 bar & 273 K that can be obtained from 1 litre of such a sample when it decomposes according to

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

- Volume Strenght of H_2O_2 solution = $11.35 \times$ molarity

PERCENTAGE LABELLING OF OLEUM

Labelled as '% oleum' means maximum amount of H_2SO_4 that can be obtained from 100 gm of such oleum (mixture of H_2SO_4 and SO_3) by adding sufficient water. For example, 109% oleum sample means, with the addition of sufficient water to 100 gm oleum sample 109 gm H_2SO_4 is obtained.

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

x = mass of H_2O required for the complete conversion of SO_3 in H_2SO_4

- % of free SO_3 in oleum = $\left(\dfrac{40}{9} \times x\right)\%$

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.

   $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

   1 vol. 3 vol. 2 vol.

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

   The stoichiometric coefficients of a balacned chemical reactions 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.

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

   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 an 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_2Cl_2	CO
Turpentine oil	O_3
Alkaline pyrogallol	O_2
water	NH_3, HCl
$CuSO_4/CaCl_2$	H_2O

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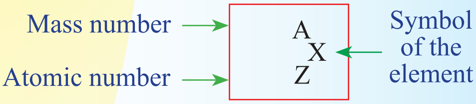
CHAPTER 2

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: ${}_6C^{12}$, ${}_6C^{13}$, ${}_6C^{14}$
- **Isobars:** Same mass number but different atomic number

  Example: ${}_1H^3$, ${}_2He^3$
- **Isodiaphers:** Same difference of number of Neutrons & protons

  Example: ${}_5B^{11}$, ${}_6C^{13}$

- **Isotones:** Having same number of neutron

  Example: ${}_1H^3$, ${}_2He^4$
- **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.

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

- RW → MW → IR → Visible → UV → X-ryas → CR (Radiowaves → Microwaves → Infrared rays → Visible rays → Ultraviolet rays → X-rays → Cosmic rays)
- Wavelength decreases →
- Frequency increases →
- $c = \nu\lambda$ $\quad$ $\lambda = \dfrac{c}{\nu}$ $\quad$ $\bar{\nu} = \dfrac{1}{\lambda} = \dfrac{\nu}{c}$

  $T = \dfrac{1}{\nu}$ $\quad$ $E = \dfrac{hc}{\lambda} = h\nu,\ h = 6.626 \times 10^{-34}$ Js

  $E(ev) = \dfrac{12400}{\lambda(\mathring{A})}$
- Total amount of energy transmitted $E = nh\nu = \dfrac{nhc}{\lambda}$

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:** $r = 0.529 \times \frac{n^2}{Z} \text{Å}$
- **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

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

  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.

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

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

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

  $1 \text{ eV} = 3.8\,3 \times 10^{-23}$ kcal

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

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

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

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

$$r = \frac{n^2h^2}{4\pi^2 mkze^2}$$

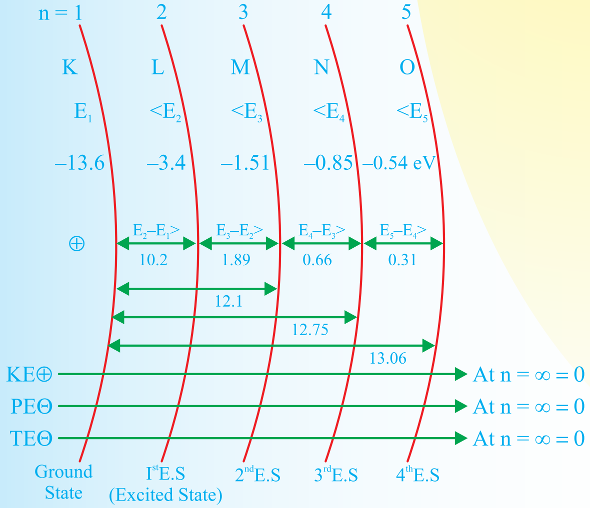
$$E = \frac{2\pi^2 mz^2e^4k^2}{n^2h^2}$$

HYDROGEN SPECTRUM

- **Rydberg's Equation:**

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

  $R_H \cong 109700\ \text{cm}^{-1}$ = 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 v, least E
- Similarly H_β line means $n_2 = n_1 + 2$
- When electron de-excite 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-excite 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 posses 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) $\cong \sqrt{\frac{150}{V(vols)}}$Å
- $\lambda = \frac{h}{\sqrt{2mKE}}$

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.
- $\Delta x.\Delta p \geq \frac{h}{4\pi}$ 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)**

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

  ⇒ Values n = 1, 2, 3, 4, 5 …

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

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

  ⇒ Total number of orbitals in an orbit = n^2

  ⇒ 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

  ⇒ Values ⇒ 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 = 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

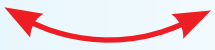
  ⇒ Indicates orientation of orbital i.e. direction of electron density.

  ⇒ Value of m = –*l* ....0.............+*l*

  ⇒ Maximum no of e's in an orbital = 2
  (with opposite spin)

m for p sub shell = p_x p_y p_z

–1 +1 0



m for d sub shell =

d_{xy} d_{yx} d_{z^2} d_{xz} $d_{x^2-y^2}$

–2 –1 0 +1 +2

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

Given by Uhlenback & Goudsmit

Values of s = ±½

Total value of spin in an atom = ±½ × 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.
  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10}$
- **(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.

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CHAPTER 3

Gaseous State

GAS LAW

Boyle's law:

$$V \propto \frac{1}{P}(n, T = \text{const}) \boxed{P_1V_1 = P_2V_2}$$

Charle's law:

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

Gay lussac's law:

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

Avogadro's law:

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

Ideal gas equation $PV = nRT$

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

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

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

GRAHAM'S DIFFUSION LAW

It is applicable for non reacting gases

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

$$VD = \frac{d_{gas}}{d_{H_2}} = \frac{M_w}{2}$$

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 : $PV = 1/3\ mN\ V^2_{rms}$	
Dalton's Law of Partial Pressure	**Average Kinetic Energy (KE_{av})**
$P_{mixture} = \underbrace{P_1 + P_2 + P_3}_{\text{Partial pressure}}.....$(T & V const.) $P_{moist\ gas} = P_{dry\ gas} + P_{water\ vapours}$ It is applicable for non reacting gases. Methods of determination of partial pressure (P_A & P_B are partial pressure) ● From ideal gas equation $P_AV = n_A RT$ & $P_BV = n_B RT$ ● In the form of mole fraction. $P_A = X_AP_T = \frac{n_A}{n_t}P_T$; $P_B = X_BP_T = \frac{n_B}{n_t}P_T$ $[X_A + X_B = 1]$ P_T = sum of partial pressure of all gases ● In the form of volume fraction. $P_A = \frac{V_A}{V}P_T$ & $P_B = \frac{V_B}{V}P_T$ ● If individual pressure and individual volume are given $P_A = \frac{V_A}{V}P_1$ and $P_B = \frac{V_B}{V}P_2$ P_1, P_2 = pressure of gases before mixing P_A, P_B = pressure of gases after mixing	$KE_{av} = \frac{3}{2}nRT$ (n moles) $KE_{av} = \frac{3}{2}RT$ (1 mol or N_A molecules) $KE_{av} = \frac{3}{2}KT$ (1 molecule) $K = 1.38 \times 10^{-23}\ JK^{-1}\ molecule^{-1}$ K is called Boltzman's constant $v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + ...v_n^2}{N}}$ $v_{av} = \frac{v_1 + v_2 + v_3...v_n}{N}$ $v_{rms} = \sqrt{\frac{3RT}{Mw}}$ $v_{av} = \sqrt{\frac{8}{\pi}\frac{RT}{Mw}}$ $v_{mp} = \sqrt{\frac{2RT}{Mw}}$ $v_{rms} = \sqrt{\frac{3PV}{Mw}}$ $v_{av} = \sqrt{\frac{8}{\pi}\frac{PV}{Mw}}$ $v_{mp} = \sqrt{\frac{2PV}{Mw}}$ $v_{rms} = \sqrt{\frac{3P}{d}}$ $v_{av} = \sqrt{\frac{8}{\pi}\frac{P}{d}}$ $v_{mp} = \sqrt{\frac{2P}{d}}$ $v_{rms} : v_{av} : v_{mp} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2}$ $= 1 : 0.92 : 0.82$ $v_{mp} : v_{av} : v_{rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$ $= 1 : 1.128 : 1.224$ Compressibility factor $(z) = \frac{(V_m)obs}{V_I} = \frac{P(V_m)obs}{RT}$ 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.

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↑, imcompressible vol.↑, compressible vol. ↓	• At high pressure, Vanderwaal's eq^n is $\boxed{PV_m - Pb = RT}$ • At low pressure or Moderate pressure vanderwaal's eq^n 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.

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CHAPTER 4

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 = const.	**Isochoric** V = const.	**Isobaric** P = const.	**Adiabatic** No heat exchange dq = 0	**Cyclic** Initial & final state of system are same

Reversible process	Irreversible process
• Slow process • At any time system and surrounding are in equilibrium. • $P_{sys} = P_{surr} \pm dP$	• Fast process • No equilibrium between system and surrounding • $P_{sys} = P_{surr} \pm \Delta P$

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

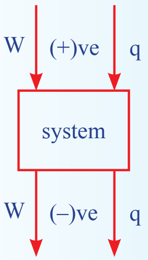
General values of C_V & C_P for an ideal gas can be taken as follows.

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	4	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non Linear	3	3	3	3R	6R	4R	7R	$\frac{4}{3}$	$\frac{7}{6}$

WORK (W)

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

SIGN CONVENTION



INTERNAL ENERGY (E & U)

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

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

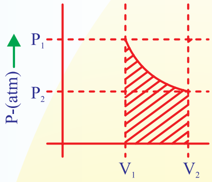
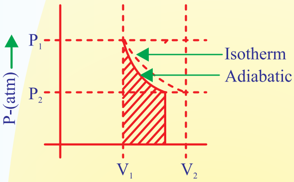
FIRST LAW OF THERMODYNAMICS

Law of conservation of energy

$$\boxed{\Delta U = q + W}$$

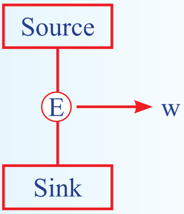
ENTHALPY

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

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	$w = nC_V(T_2 - T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	$q = 0$ $PV^{\gamma} = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$	

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.

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

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

$\Delta S_{syt} + \Delta S_{surr} \geq 0$ (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 crytalline substance is zero". which means that at absolute zero every crystalline solid is in a sate 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

$$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_P)_r (T_2 - T_1)$$ **{Kirchhoff'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)

BOND ENTHALPY

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

$\Delta_r H$ = (Sum of bond enthalpy of gaseous reactant) – (Sum of bond enthalpy of gaseous product)

RESONANCE ENERGY

$$\Delta H^\circ_{\text{resonance}} = \Delta_f H^\circ \text{ (experimental)} - \Delta_f H^\circ \text{ (calculated)}$$
$$= \Delta_C H^\circ \text{ (calculated)} - \Delta_C H^\circ \text{ (experimental)}$$

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.

SA + SB → salt + water ; $\Delta H^\circ_{\text{neut}}$

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$; $\Delta H = -13.7 \text{ kCal eq}^{-1} = 57.3 \text{ kJ eq}^{-1}$

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

NOTES

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

$$\Delta_r H = \Sigma(\Delta H_C)_{\text{reactant}} - \Sigma\ (\Delta H_C)_{\text{product}}$$

(b) For heat of formation

$$\Delta_r H = \Sigma(\Delta H_f)_{\text{product}} - \Sigma\ (\Delta H_f)_{\text{reactant}}$$

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CHAPTER 5

Chemical Equilibrium

Consider a reversible reaction,

$$aA + bB \underset{r_b}{\overset{r_f}{\rightleftharpoons}} cC + dD$$

AT EQUILIBRIUM STATE

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

So, at equilibrium,

$$K_C = \frac{[C]^C[D]^d}{[A]^a[B]^b} = \frac{K_f}{K_b} \qquad \text{In terms of active mass}$$

$$K_P = \frac{[P_C]^C[P_D]^d}{[P_A]^a[P_B]^b} \qquad \text{In terms of partial pressure}$$

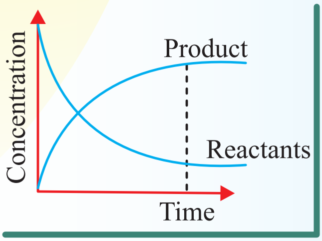
$$K_X = \frac{[X_C]^C[X_D]^d}{[X_A]^a[X_B]^b} \qquad \text{In terms of mole fraction}$$

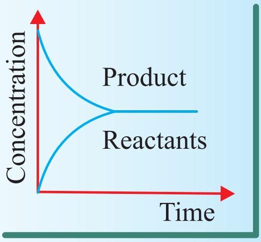
$$K_P = K_C(RT)^{\Delta n_g}$$

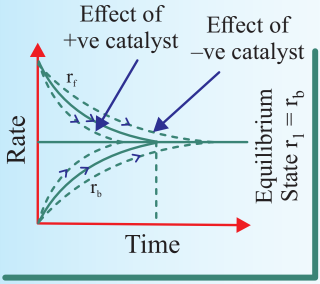
While determining Δn_g take only gaseous species.

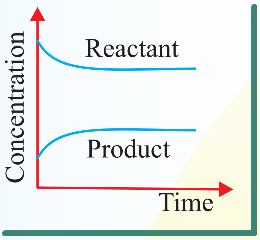
The active mass of solid & pure liquid is a constant quantity (unity) because it is an intensive property.

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:

$$aA + bB \rightleftharpoons cC + dD$$

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

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

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) ↑ [A] (ii) ↓ [A]	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
Pressure	(i) ↑ in pressure (ii) ↓ in pressure	Unchanged Unchanged	Backward direction Forward direction	Forward direction Backward direction
Temperature	(i) ↑ in Endothermic (ii) ↑ in Exothermic	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
Dissociation	(i) ↑ in pressure (ii) ↑ in volume	Unchanged Unchanged	Dissociation Decreases Dissociation Increases	Dissociation Increases Dissociation Decreases
Mixing of inert gas	(i) at constant P (ii) at constant V	Unchanged Unchanged	Dissociation Increases Unchanged	Dissociation Decreases Unchanged

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

$\Delta G = \Delta G° + RT \ln Q$ …(i) where, $\Delta G°$ = 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

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

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

Case II: If $\Delta G° > 0$, then $(-\Delta G°/RT)$ is negative, i.e., $e^{(-\Delta G°/RT)} < 1$, 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.

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CHAPTER 6

Ionic Equilibrium

ACID

- **Strong**
  - $HClO_4$
  - HI
  - HBr
  - H_2SO_4
  - HCl
  - HNO_3
- **Weak**
  - $HClO_3$
  - $HClO_2$
  - HClO
  - H_3PO_4
  - H_3PO_2
  - H_3PO_2
  - H_2S

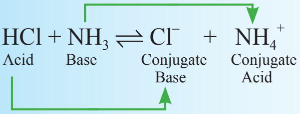
  - H_2CO_3
  - HNO_2
  - H_2SO_3
  - HCN
  - H_3BO_3
  - HF
  - Almost all organic acid

    Like: [acetic acid, oxalic acid]

BASE

- **Strong**
  - Group-1 hydroxide except-LiOH
  - NaOH
  - KOH
  - RbOH
  - Group-2 hydroxide except $Be(OH)_2$ and $Mg(OH)_2$
  - $^{**}Ca(OH)_2$
  - $Sr(OH)_2$
  - $Ba(OH)_2$
- **Weak**
  - All other bases like
  - NH_4OH
  - $Zn(OH)_2$
  - $Al(OH)_3$
  - $Fe(OH)_3$
  - $Cu(OH)_2$
  - etc.

ACID BASE THEORIES (Arrhenius Concept)	
Acid	**Base**
Which produce H^+ ion in aqueous solution. e.g. HCl, H_2SO_4, $HClO_4$, H_3PO_4, CH_3COOH but **H_3BO_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  $\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NH_3} \rightleftharpoons \underset{\text{Conjugate Base}}{Cl^-} + \underset{\text{Conjugate Acid}}{NH_4^+}$ **Major Limitation:** Does not explain acidic behaviour of aprotic acids e.g. SO_2, CO_2, $AlCl_3$, $SiCl_4$	• 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^+) $H_2O \rightleftharpoons H^+ + OH^-$ $H_2O + H^+ \rightleftharpoons H_3O^+$

LEWIS THEORY			
ACID		**BASE**	
TYPES OF LEWIS ACID		**TYPES OF LEWIS BASE**	
Lewis acid is an electron pair acceptor.		**Lewis base is an electron pair donor.**	
1.	**Having Incomplete octet:** BF_3, BCl_3, $B(OH)_3$, $AlCl_3$ etc.	**1.**	**Neutral molecule having lone pair** $\underset{\cdot\cdot}{\ddot{N}}H_3$, $R-\ddot{N}H_2$, $R_2-\ddot{N}H$, $H-\underset{\cdot\cdot}{\ddot{O}}-H$, $R-\underset{\cdot\cdot}{\ddot{O}}-R$ 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_3COO^- etc. • 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_3O^+, PH_4^+ etc.		

OSTWALD'S DILUTION LAW	
OSTWALD'S DILUTION LAW (Only for weak electrolytes) $\alpha \propto \sqrt{\text{dilution}}$ dilution $\uparrow \Rightarrow \alpha \uparrow$ **EXPLANATION OF WATER** $H_2O \rightleftharpoons H^+ + OH^-$ K_w = Ionic product of water $pK_w = pH + pOH$ K = dissociation constant of water $K = \frac{K_w}{[H_2O]} [\because [H_2O] = 55.5]$	**FOR PURE WATER** 1. $[H^+] = [OH^-]$ 2. $pH = pOH$ 3. $(pH)_{\text{pure water}} = \frac{pK_w}{2}$ • pH of an acidic solution is always less than pH of pure water. • pH of an 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	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2}[pK_w + pK_a + \log C]$

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

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, CH_3COONH_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, $CH_3COOH + CH_3COONa$. 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, $NH_4OH + NH_4Cl$. They have the pH value more than 7.
- pH of an acidic buffer:

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} = pK_a + \log \frac{[Conjugate\ base]}{[Acid]}$$

(Henderson - Hasselbalch equation)

- pH of an basic buffer:

$$pOH = pK_b + \log \frac{[Salt]}{[Base]} = pK_b + \log \frac{[Conjugate\ acid]}{[Base]}$$

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

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

Buffer	Buffer range in pH
Acidic	$pK_a \pm 1$
Basic	$(pK_w - pK_b) \pm 1$

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.

$$\boxed{\mathrm{AgCl(s)} \underset{\text{dissolution}}{\rightleftharpoons} \mathrm{AgCl(aq)} \underset{\text{dissociation}}{\longrightarrow} \mathrm{Ag^+ + Cl^-}}$$

Solubility Product (K_{sp})

$$\mathrm{AgCl} \rightleftharpoons \mathrm{Ag^+ + Cl^-}$$

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

depends only on temperature.

Expressions of K_{sp} : $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

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

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

Ionic Product [Q_{sp}]

$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$; $Q_{sp}[A^{y+}]^x\,[B^{x-}]^y$

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

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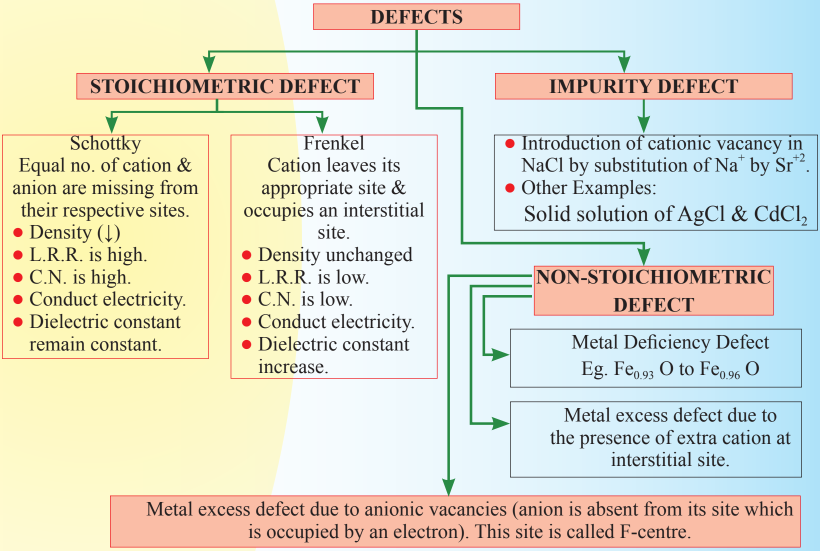
CHAPTER 7

Solid State



DEFECTS

STOICHIOMETRIC DEFECT

Schottky
Equal no. of cation & anion are missing from their respective sites.

- Density (↓)
- L.R.R. is high.
- C.N. is high.
- Conduct electricity.
- Dielectric constant remain constant.

Frenkel
Cation leaves its appropriate site & occupies an interstitial site.

- Density unchanged
- L.R.R. is low.
- C.N. is low.
- Conduct electricity.
- Dielectric constant increase.

IMPURITY DEFECT

- Introduction of cationic vacancy in NaCl by substitution of Na^+ by Sr^{+2}.
- Other Examples:
  Solid solution of AgCl & $CdCl_2$

NON-STOICHIOMETRIC DEFECT

Metal Deficiency Defect
Eg. $Fe_{0.93}O$ to $Fe_{0.96}O$

Metal excess defect due to the presence of extra cation at interstitial site.

Metal excess defect due to anionic vacancies (anion is absent from its site which is occupied by an electron). This site is called F-centre.

Density

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

CONTRIBUTION	
AT CORNER	1/8
AT FACE	1/2
AT EDGE	1/4
AT BODY CNETRE	1

CORNERS	8
FACES	6
EDGES	12
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
$0.155 \le r/R < 0.225$	3	Plane Trigonal	—	—	—	Boron oxide (B_2O_3)
$0.225 \le r/R < 0.414$	4	Tetrahedral	FCC,HCP	On body diagonal at $\sqrt{3}a/4$ distance from corner of the unit cell	2	ZnS, SiO_2, Na_2O, CaF_2
$0.414 \le r/R < 0.732$	6	Octahedral	FCC, HCP	Body centre & edge centre	1	NaCl, MgO
$0.732 \le r/R < 1.000$	8	Cubical	SCC	Body centre	1	CsCl

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

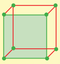
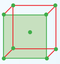
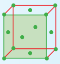
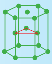
CRYSTALLINE
These solids have definite characteristic shape
Definite melting point & heat of fusion
Cleavage surfaces are smooth
Anisotropic in nature.
Long range order.
Ex.: NaCl, Quartz, Metal, Diamond etc.

AMORPHOUS
These solids have irregular shape.
Indefinite melting point & heat of fusion.
Cleavage surface are irregular.
Isotropic in nature.
Short range order.
Ex. Glass, Quartz Glass, Rubber, Plastics etc.

Name of system	Axial	Axial angle	Bravais Lattices
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	SCC, BCC, FCC
2. Tetragonal	$a = b \ne c$	$\alpha = \beta = \gamma = 90°$	SCC, BCC
3. Orthorhombic or Rhombic	$a \ne b \ne c$	$\alpha = \beta = \gamma = 90°$	SCC, BCC, FCC, ECC
4. Monoclinic	$a \ne b \ne c$	$\alpha = \gamma = 90°, \beta \ne 90°$	SCC,ECC
5. Triclinic	$a \ne b \ne c$	$\alpha = \beta \ne \gamma \ne 90°$	SCC
6. Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \ne 90°$	SCC
7. Hexagonal	$a = b \ne c$	$\alpha = \beta = 90°, \gamma = 120°$	SCC

S. No.	Type of Ionic Crystal	Geometry	Coordination Number	No. of formula per U.C.	Examples
1.	NaCl (1:1) (Rock salt Type)	CCP → Cl^-: Every element of CCP → Na^+: At Every OHV	6 : 6	$4Na^+ + 4Cl^-$ 4NaCl (4)	● Halides of (Li, Na, K, Rb); Oxides & sulphides of ● Alkaline earth metals; (some exception) ● AgF, AgCl, AgBr, NH_4X
2.	CsCl Type (1 : 1)	BCC Type → Cl^-: At Every Corner → Cs^+: At Body centre	8 : 8	$1Cs^+ + 1Cl^-$ 1CsCl (1)	● 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)	CCP → S^{-2}: Every element of CCP CCP → 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)	CCP → Ca^{+2}: Every element of CCP CCP → F^-: At every THV	$4Ca^{+2}$ $8F^-$ 8 : 4	$4Ca^{+2} + 8F^{-1}$ $4CaF_2$ (4)	$BaCl_2$, BaF_2, $SrCl_2$, SrF_2, $CaCl_2$, CaF_2
5.	Na_2O Type (2:1) (Antifluorite Type)	CCP → Na^+: At every THV CCP → O^{-2}: Every element of CCP	$8Na^+$ $4O^{-2}$ 4 : 8	$8Na^+ + 4O^{-2}$ $4Na_2O$ (4)	Li_2O, Li_2S, Na_2O Na_2S, K_2O, K_2S
6.	ZnS type (1:1) (Wurtzite) another geometry of ZnS	HCP → S^{-2}: Every Element of HCP HCP → 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

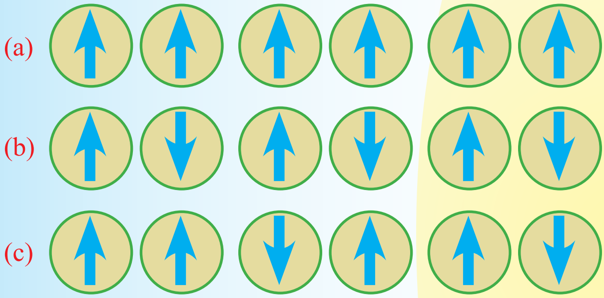
MAGNETIC PROPERTIES

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., O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}.
- Diamagnetic substances are weakly repelled by a magnetic field. They have no unpaired electrons and hence have zero magnetic moment, e.g., H_2O, NaCl and C_6H_6.

- 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

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CHAPTER 8

Solutions

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

$T\uparrow \Rightarrow$ V.P.$\uparrow$

Attractive Forces$\uparrow \Rightarrow$ V.P. $\downarrow$

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

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

$$P_A = \text{P}_\text{A}^\circ \text{X}_\text{A}$$

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

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

(1) Relative lowering of V.P. :

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

where n_B = mole of Non-volatile solute.

i = Vant Hoff's factor.

(2) Elevation in B.P. :

$$\Delta T_b = (T_b' - T_b) = i.\,K_b \times m.$$

where $K_\text{b} = \dfrac{\text{RT}_b^2}{1000 \times l_v}$

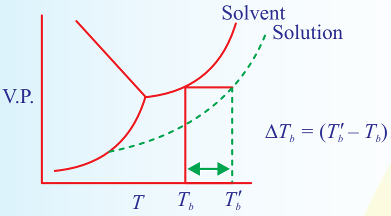
where T_b = B.P. of pure solvent.

l = Latent heat of vapourization per gm

K_b = molal elevation constant

M = Molar mass

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



(3) Depression in FP.

$$\Delta T_f = T_f - T_f' = i\,k_f \times m$$

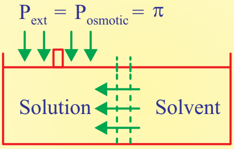
where $k_f = \dfrac{RT_f^2}{1000 \times \ell_f}$

T_f = f.p. of pure solvent

k_f = molal depression constant

l_f = latent heat of fusion per gm.

(4) Osmotic pressure:



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

$$\pi = iC.\ S.T.$$

where π = osmotic pressure

C = molarity (mole/lit)

$S = R$ = const. for solution.

Sol. (1)   Sol (2)

If $\pi_1 = \pi_2$ Isotonic

If $\pi_1 > \pi_2$ $\begin{cases} \text{sol}^n\,(1) \text{ hypertonic} \\ \text{sol}^n\,(2) \text{ hypotonic} \end{cases}$

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, $BaCl_2$	$\underset{1-x}{A_2B} \rightleftharpoons \underset{2x}{2A^+} + \underset{x}{B^{2-}}$	3	(1 + 2x)	$\dfrac{m_1}{(1+2x)}$

Solute	Example	Ionisation/ association (x degree)	y*	Van't Hoff factor	Abnormal mol. wt. (m_1')
Electrolyte	$K_3[Fe(CN)_6]$,	$\underset{1-x}{A_2B} \rightleftharpoons \underset{x}{A^{3+}} + \underset{3x}{3B^-}$	4	(1 + 3x)	$\frac{m_1}{(1+3x)}$
A_2B, AB_3	$FeCl_3$				
Associated Solute	benzoic acid in benzene	$2A \rightleftharpoons A_2$	$\frac{1}{2}$	$\left(1-\frac{x}{2}\right) = \left(\frac{2-x}{2}\right)$	$\frac{2m_1}{(2-x)}$
	forming dimer	$\underset{(1-x)}{A} \rightleftharpoons \frac{1}{2}\underset{x/2}{A_2}$			
	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	$\underset{(1-x)}{A} \rightleftharpoons \frac{1}{n}\underset{x/2}{A_n}$			
General	one mole of solute giving y mol of products	$A \rightleftharpoons yB$	y	[1 + (y −1) x]	$\frac{m_1}{[1+(y-1)x]}$

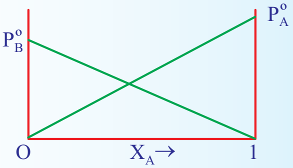
*** number of products form one mole solute**

Raoult's Law

(1) Volatile binary liquid mix:

Volatile liq.	A	B
Mole fraction	X_A / Y_A	X_B / Y_B ⇒ liq/vapour
V.P. of pure liq.	P_A^o	P_B^o

Binary liquid solution:

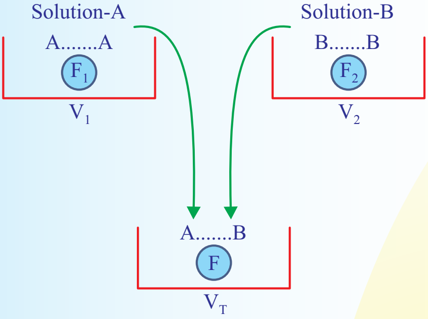


By Raoult's law ⇒ $P_T = P_A^o X_A + P_B^o X_B = P_A + P_B$ ......(i)

By Dalton's law ⇒ $P_A = Y_A P_T$ ......(ii)

$P_B = Y_B P_T$ ......(iii)

Ideal and Non-Ideal Solution



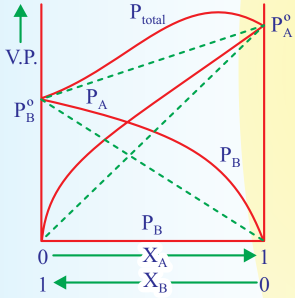
Ideal solution : $\begin{cases} F_1 \simeq F_2 \simeq F \\ V_T = V_1 + V_2 \end{cases} \Rightarrow \Delta H_{\text{solution}} = 0$

Non-Ideal Solution

(1) Solution showing +ve deviation :

$F < F_1$ & F_2

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

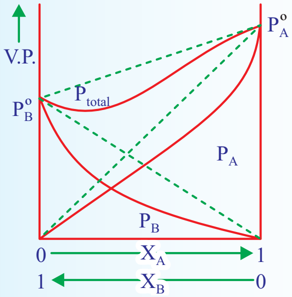


(2) Solution showing -ve deviation:

$\Rightarrow F > F_1$ & F_2

$\Rightarrow V_T < (V_1 + V_2)$

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



Deviation from Raoult's Law

	Positive deviation (ΔH = +ve)	**Negative deviation (ΔH = – ve)**	**Zero deviation (ΔH = 0)**
(*i*)	ethanol + cyclohexane	acetone + chloroform	benzene + toluene
(*ii*)	acetone + carbon disulphide n-hexane + n-heptane	benzene + chlorform	
(*iii*)	acetone + benzene	nitric acid + chloroform	ethyl bromide + ethyl iodide
(*iv*)	ethanol + acetone	acetone + aniline	chlorobenzene + bromo benzene
(*v*)	ethanol + water	water + nitric acid	
(*vi*)	carbon tetrachloride chloroform	diethyl ether + chloroform	

Azeotropic mixtures: Some liquids on mixing form azeotropes which are binary mixture having same composition in liquid and vapour phase and boil at a constant temperature. 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 soluton showing positive deviation. For example (95.5%) + water (4.5%) + water boils at 351.15 K.

(*ii*) **Maximum boiling Azeotropic mixtures:** The mixture of two liquids whose boiling point are 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.

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CHAPTER

9

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.

$$\text{Zn(s)} \mid \text{ZnSO}_4\text{(sol)} \parallel \text{CuSO}_4\text{(sol)} \mid \text{Cu(s)}$$

(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.

$$\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$$

(v) Inert electrodes are represented in the bracket

$$Zn \mid ZnSO_4 \parallel H^+ \mid H_2, Pt$$

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,

Work done = Charge × 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.

$\therefore\ \Delta G = -nFE$

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

(i) From thermodynamics we know, ΔG = 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 ΔG = 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_{cell} = reduction potential of cathode – Reduction potential of anode

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

E°_{cell} = Standard reduction potential of cathode – Standard R.P of anode

NERNST EQUATION

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

$$\Delta G = \Delta G^\circ + RT \ln Q \qquad ...(A)$$

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

$$\therefore -\Delta G = nFE \qquad \text{and} \qquad -\Delta G° = nFE°$$

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

At 25°C, above equation may be written as $E = E^0 - \frac{0.0591}{n} \log Q$

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:

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

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

$$E = E^0 - \frac{0.0591}{n} \log Q \qquad ...(i)$$

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

$\therefore$ From Eq. (i), we have

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

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

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

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

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

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 Helmoholtz equation,

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_P \qquad \text{....(ii)}$$

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:

$Pt, H_2(P_1) \mid H^+(C) \mid H_2(P_2), Pt$

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

Cell process: $1/2H_2(p_1) \rightarrow H^+(c) + e^-$ (Anode process)

$$\begin{array}{l} H^+(c) + e^- \rightarrow 1/2H_2(p_2) \\ \hline 1/2H_2(p_1) \rightleftharpoons 1/2H_2(p_2) \end{array} \qquad \therefore \; E = -\frac{2.303RT}{F}\log\left[\frac{p_2}{p_1}\right]^{1/2}$$

$$\text{or} \quad E = \left[\frac{2.303RT}{2F}\right]\log\left[\frac{p_2}{p_1}\right], \quad \text{At} 25^0 C, \; E = \frac{0.059}{2F}\log\left[\frac{p_1}{p_2}\right]$$

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

(ii) Electrolyte concentration cells:

$Zn(s) \mid ZnSO_4\,(C_1) \parallel ZnSO_4\,(C_2) \mid Zn(s)$

In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,

$Zn(s) \rightarrow Zn^{2+}\,(C_1) + 2e^-$ (Anodic process)

$$\begin{array}{l} Zn^{2+}(C_2) + 2e^- \rightarrow Zn(s) \\ \hline Zn^{2+}(C_2) \rightleftharpoons Zn^{2+}(C_1) \end{array} \qquad \text{(Over all process)}$$

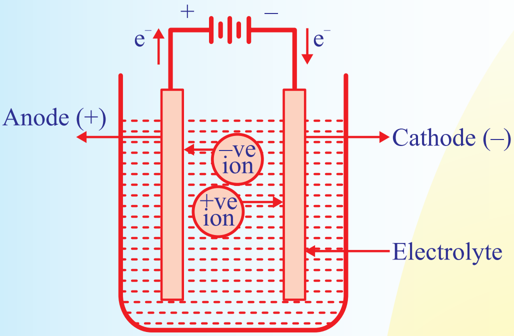
$\therefore$ From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F}\log\left[\frac{C_1}{C_2}\right] \quad \text{or} \quad E = \frac{2.303RT}{2F}\log\left[\frac{C_2}{C_1}\right]$$

For spontanity of such cell reaction, $C_2 > C_1$

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

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 coluomb

$$w = ZQ$$

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

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.

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

Specific resistance is the resistance of a conductor having lengths of 1 cm and cross sectional area of 1 cm^2.

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 cm^3 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 concern ration of electrolyte solution is expressed as C gm equivalent per liter.

   Thus, $V = \dfrac{1000}{C}$

   {Volume having 1 gm equivalent electrolyte in the solution}

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

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.

   Thus, $V = \dfrac{1000}{M}$

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

   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) A strong electrolyte containing same cation as in the test electrolyte, say HCl.

(b) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa.

(c) 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:

$$\Lambda_m^0 \text{ of } (CH_3COOH) = \Lambda_m^0\,(HCl) + \Lambda_m^0\,(CH_3COONa) - \Lambda_m^0\,(NaCl)$$

Proof:

$$\Lambda_m^0\ (HCl) = \lambda_H^0 + \lambda_{Cl^-}^0 \qquad ...(i)$$

$$\Lambda_m^0\ (CH_3COONa) = \lambda_{CH_3COO^-}^0 + \lambda_{Na^+}^0 \qquad ...(ii)$$

$$\Lambda_m^0\ (NaCl) = \lambda_{Na^+}^0 + \lambda_{Cl^-}^0 \qquad ...(iii)$$

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

$$\Lambda_m^0\ (HCl) + \Lambda_{(CH_3COONa)}^0 - \Lambda_{(NaCl)}^0 = \lambda_{(H)^+}^0 + \lambda_{(CH_3COO^-)}^0 = \Lambda_{(CH_3COOH)}^0$$

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

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

(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.

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CHAPTER 10

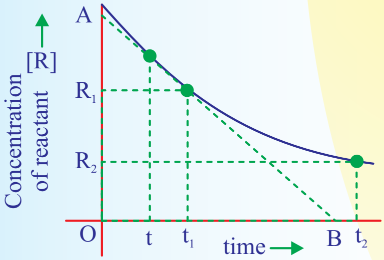
Chemical Kinetics

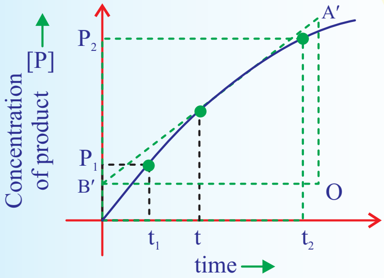
- **Rate of reaction** (ROR) $= \dfrac{\text{Rate of disappearance of reactant (appearance of products)}}{\text{Stoichiometric coefficient of reactant (products)}}$
- **For a reaction:**

  $aA + bB \rightarrow cC + dD$
- **Instantaneous rate:** $-\dfrac{1}{a}\left(\dfrac{d[A]}{dt}\right) = -\dfrac{1}{b}\left(\dfrac{d[B]}{dt}\right) = \dfrac{1}{c}\left(\dfrac{d[C]}{dt}\right) = \dfrac{1}{d}\left(\dfrac{d[D]}{dt}\right)$

  Relationship between rate of reaction and rate of disappearance of reactant (rate of appearance of product).
- **Average rate:** $-\dfrac{1}{a}\left(\dfrac{\Delta[A]}{\Delta t}\right) = -\dfrac{1}{b}\left(\dfrac{\Delta[B]}{\Delta t}\right) = \dfrac{1}{c}\left(\dfrac{\Delta[C]}{\Delta t}\right) = \dfrac{1}{d}\left(\dfrac{\Delta[D]}{d\Delta t}\right)$

  ⇒ Graphical method for determining rate:





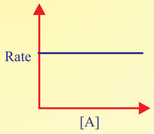
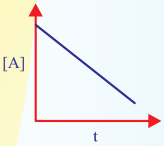
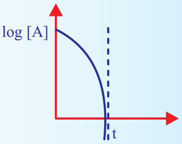
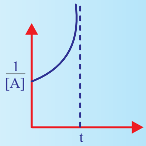
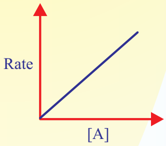
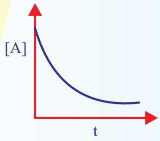
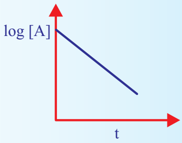
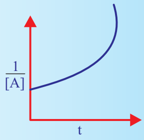
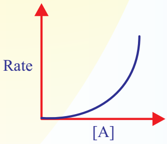
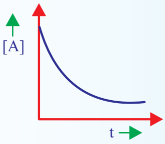
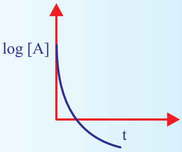
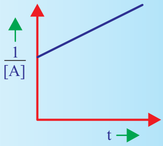
$$\text{Avg. Rate} = -\left(\frac{[R]_2 - [R]_1}{t_2 - t_1}\right) = \frac{([P]_2 - [P_1])}{t_2 - t_1}$$

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

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

$[A]_0 \Rightarrow$ initial concentration

$[A] \Rightarrow$ 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:

$$\underset{\substack{\text{Sucrose} \\ \text{dextro-rotatory} \\ (+66.5^\circ)}}{C_{12}H_{22}O_{11}\,(aq)} + H_2O \xrightarrow{H^+} \underbrace{\underset{\substack{\text{Glucose} \\ \text{dextro-rotatory} \\ (+52.5^\circ)}}{C_6H_{12}O_6\,(aq)} + \underset{\substack{\text{Fructose} \\ \text{laevo-rotatory} \\ (-92^\circ)}}{C_6H_{12}O_6\,(aq)}}_{\text{(Laevo-rotatory)}}$$

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

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:

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

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

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 be 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.

	$t = 0$	$t = t$	$t = 2t$	$t = 3t.....$
Reactant conc.	a_0	a_0x	a_0x^2	$a_0x^3.....$

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

- Graph of In [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.

$t = 0$	$t = t$	$t = 2t$	$t = 3t.....$
C_0	$C_0 - x$	$C_0 - 2x$	$C_0 - 3x....$

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

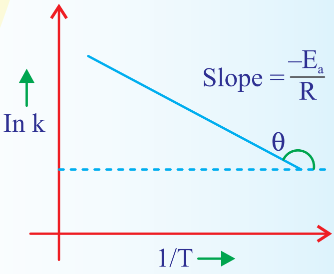
A zero order reaction finishes in $\boxed{t = \frac{[A]_0}{k}}$

Temperature dependence

- Arrhenious equation : $k = A.e^{-E_a/RT}$
- 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 then E_a.
- A and E_a are constant i.e. do not vary with temperature

$$\text{In } k = \text{In } A - \frac{E_a}{RT}$$

Graph: Graphical determination of E_a.

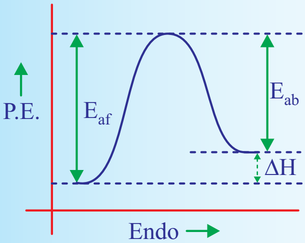


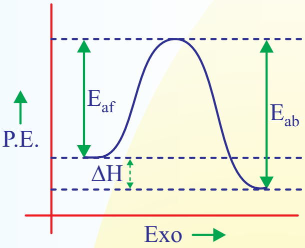
$$\text{Temperature coefficient} = \frac{k_{T+10}}{k_T}$$

By default T = 298K

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

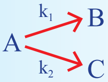
Endothermic and exothermic reactions:





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

Parallel reaction:



(*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 → 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 → CATALYST

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CHAPTER 11

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

$$[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^{-}$$

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.

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

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***.

NOTES

Gelatin and startch have the maximum & minimum protective power.

$$\text{Protection Capacity } \alpha \frac{1}{\begin{array}{c}\text{Protection Number}\\ \text{(Gold number)}\end{array}}$$

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.

$$AgI / I^+$$

- 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.

$$AgI / I^-$$

Positively Charged Sols	Negatively Charged Sols
Hydrated metallic oxides. e.g., $Al_2O_3 . xH_2O$, $Fe_2O_3 . xH_2O$, metal hydroxides, $Fe(OH)_3$, $Al(OH)_3$, 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.

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CHAPTER

12

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

($\overset{\oplus}{N}H_4$ and $H_3O^{\oplus}$ are not electrophile)

Nucleophiles are electron rich species.

e.g. $Cl^{\ominus}$, $\overset{\ominus}{C}H_3$, $\overset{\ominus}{O}H$, $RO^{\ominus}$,$\overset{\ominus}{C}N$, $\ddot{N}H_3$, $R\underset{\cdot\cdot}{\ddot{O}}H$, $CH_2{=}\ CH_2$, $CH{\equiv}CH$

Relative electron withdrawing order (–I order)

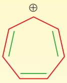
$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -COOH > -X > -OR > -OH$
$> -C{\equiv}CH > -NH_2 > -C_6H_5 > -CH = CH_2$

Relative electron releasing order (+I order)

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

RELATIVE STABILITY ORDER

(A) Stability of carbocation


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

$(CH_3)_2\,\overset{\oplus}{C}H > CH_3\,\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2 = \overset{\oplus}{C}H > CH \equiv \overset{\oplus}{C}$

(B) Stability of free radical

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

(C) Stability of carbanion

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

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

- **Basic strength of amine:**

  In aqueous medium

  $R \Rightarrow -CH_3$ $2° > 1° > 3° NH_3$

  $R \Rightarrow -CH_2CH_3$ $2° > 3° > 1° NH_3$

  In gaseous medium

  $R \Rightarrow -CH_3$ $3° > 2° > 1° NH_3$

  $R \Rightarrow -CH_2CH_3$ $3° > 2° > 1° NH_3$

- **Reactivity towards nucleophile (NAR)**

  (1) $HCHO > CH_3CHO > (CH_3)_2CO$

  (2) $CCl_3CHO > CHCl_2CHO > CH_2ClCHO$

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

  Acid chloride > anhydride > ester > amide

- **Order of electronic effect**

  Mesomeric > Hyperconjugation > Inductive effect

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

  $R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > \underset{\text{trans form}}{RCH{=}CHR} > \underset{\text{cis form}}{RCH{=}CHR}$

  $RCH{=}CH_2 > CH_2{=}CH_2$

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

ACIDIC STRENGTH $\propto$ STABILITY OF CONJUGATE BASE

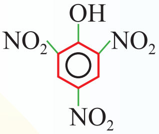
$$\propto K_a \propto \frac{1}{pK_a}$$

(i) $H_2O > CH \equiv CH > NH_3$

(ii) $CH \equiv CH > CH_2 = CH_2 > CH_3{-}CH_3$

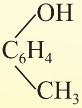
(iii) $RSO_3H > R{-}COOH >$  $> R{-}OH$

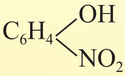
(iv) $HCOOH > CH_3COOH > CH_3CH_2COOH$

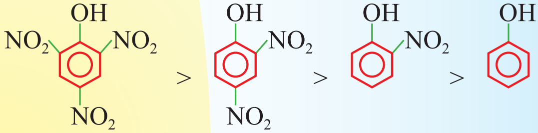
(v)  > HCOOH > C_6H_5COOH > CH_3COOH

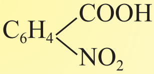
(vi) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$

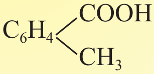
(vii) 
$$\underset{\displaystyle F}{CH_3\text{–}CH_2\text{–}CH\text{–}COOH} > \underset{\displaystyle F}{CH_3\text{–}CH\text{–}CH_2COOH} > \underset{\displaystyle F}{CH_2\text{–}CH_2CH_2COOH}$$

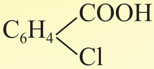
(viii) 
$C_6H_4\begin{array}{l}\diagup OH\\ \diagdown CH_3\end{array}$ Phenol > m > p > o

(ix) 
$C_6H_4\begin{array}{l}\diagup OH\\ \diagdown NO_2\end{array}$ p > o > m > Phenol

(x) 

(xi) 
$C_6H_4\begin{array}{l}\diagup COOH\\ \diagdown NO_2\end{array}$ o > p > m > benzoic acid

(xiii) 
$C_6H_4\begin{array}{l}\diagup COOH\\ \diagdown CH_3\end{array}$ o > benzoic acid > m > p

(xiv) 
$C_6H_4\begin{array}{l}\diagup COOH\\ \diagdown Cl\end{array}$ o > m > p > benzoic acid

PURIFICATION METHODS (Distillation Techniques)

Type:

(A) Simple Distillation

Conditions

(i) When liquid sample has non volatile impurities.

(ii) When boiling point difference is 30 K or more.

Examples

(i) 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.

P	$=$	P_1	$+$	P_2
Vapour pressure		Vapour pressure of Organic liquid		Vapour pressure of water

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 $+FeCl_3+\text{conc. } HCl \rightarrow Fe_4[Fe(CN)_6]_3$ Prussian blue colour
Sulphur	$2Na+S$ $\Delta\downarrow$ Na_2S	(i) $Na_2S+Na_2[Fe(CN)_5NO]$ sodium nitrosorpuside $\rightarrow Na_4[Fe(CN)_5NOS]$ a deep violet colour (ii) $Na_2S+CH_3COOH+(CH_3COO)_2Pb\rightarrow$ A black ppt. ($PbS\downarrow$)
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

Extimation of carbon and hydrogen-Leebig's method

$$C_xH_y + \underset{\text{excess}}{O_2} \rightarrow xCO_2 + y/2\ H_2O$$

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

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

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 CO_2 gas. The mixture of gases is collected over potassium hydroxide solution in which CO_2 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. H_2SO_4 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

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

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 rign (pyridine, quinole etc.) Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.

❑❑❑

CHAPTER 13

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.

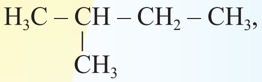
Types of Structural Isomerism

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.

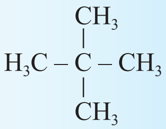
e.g. C_5H_{12}: $CH_3-CH_2-CH_2-CH_2-CH_3$

n-pentane



$$H_3C-\underset{\substack{|\\CH_3}}{CH}-CH_2-CH_3,$$

iso-pentane



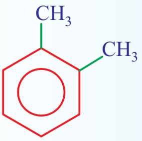
$$H_3C-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}-CH_3$$

neo-pentane

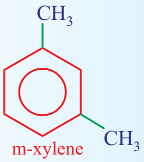
Positional isomerism: It occurs when functional groups or multiple bonds or substituents are in different positions on the same carbon chain.

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

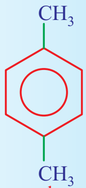
e.g. $C_6H_4(CH_3)_2$:



o-xylene ,



m-xylene ,



p-xylene

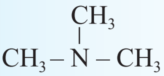
Functional isomerism: It occurs when compounds have the same molecular formula but different functional groups.

e.g. C_3H_9N: $CH_3-CH_2-CH_2-NH_2$,

1-propanamine

$CH_3-CH_2-NH-CH_3$,

N-methylethanamine



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{N}-CH_3$$

N, N-dimethylmethanamine

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

e.g. $C_4H_{10}O$: $CH_3-O-CH_2-CH_2-CH_3$

n-propyl methylether

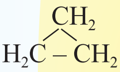
$CH_3-CH_2-O-CH_2-CH_3$

diethyl ether

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

e.g. C_3H_6: $CH_3-CH=CH_2$

propene

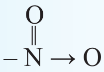


cyclopropane

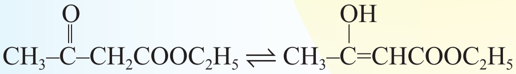
- For chain, positional and metamerism, functional group must be same.
- Metameris may also show chain and position isomeris but priority is given to metamerism.

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:

(i) Presence of  $-\overset{\overset{\displaystyle O}{\|}}{C}-$ or  $-\overset{\overset{\displaystyle O}{\|}}{N}\rightarrow O$

(ii) Presence of at least one α-H atom which is attached to a saturated C-atom.

e.g. Acetoacetic ester. 

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CHCOOC_2H_5$$

keto form enol form

Enol content enhance by:

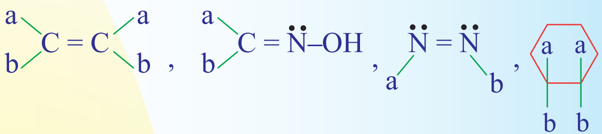
- Acidity of α-H of keto form
- Intra molecular H-Bonding in enol form
- Resonance in enol form
- Aromatisation in enol form

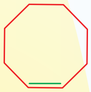
(B) STEREOISOMERISM

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

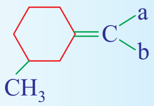
Types of Stereoisomerism

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



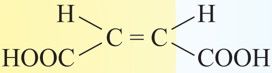


(Ring greater than 7 member with double bond)

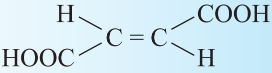


- **Cis-trans isomerism:** The cis compound is the one with the same groups on the same side of the bond, and the trans has the same groups on the opposite sides. Both isomers have different physical and chemical properties.

e.g.



cis
maleic acid



trans
fumaric acid

- 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 isomersim.

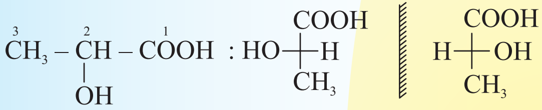
Types of optical isomers

(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)



$$\overset{3}{C}H_3-\underset{OH}{\overset{2}{C}H}-\overset{1}{C}OOH : \begin{array}{c} COOH \\ HO-\!\!+\!\!-H \\ CH_3 \end{array} \quad \Big| \quad \begin{array}{c} COOH \\ H-\!\!+\!\!-OH \\ CH_3 \end{array}$$

- **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

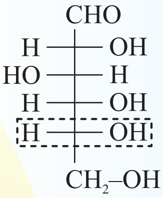
DETERMINATION OF D/L SYSTEM

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

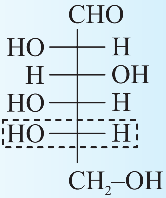
Rule: Arrange parent carbon chain the vertical line

- 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



D-Glucose



L-Glucose

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 2^{nd} atom or subsequent atoms in group.

(iv) If there is a double bond or triple bond, both atoms are considered to the 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

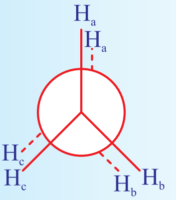
The compound	Optically active forms	Optically inactive forms (meso)
Unsymmetrical	2^n	Zero
Symmetrical If n = even	$2^{(n-1)}$	$2^{\frac{n}{2}-1}$
Symmetrical If n = odd	$2^{(n-1)} - 2^{(n-1)/2}$	$2^{(n-1)/2}$

* Where n = no. of chiral carbon

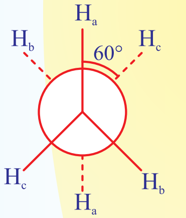
The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by 0-360° are called conformations or conformational isomers or rotational isomers and this phenomenon is called conformational isomers.

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.

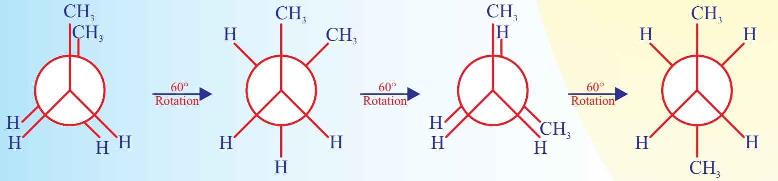


Eclipsed from (least stable)



Staggered form (most stable)

- **Conformations of butane:** $\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{2}{C}H_2 - \overset{1}{C}H_3$



Fully eclipsed (less stable) | Gauche (more stable) | Partially Eclipsed form | Anti Staggered-form (most stable)

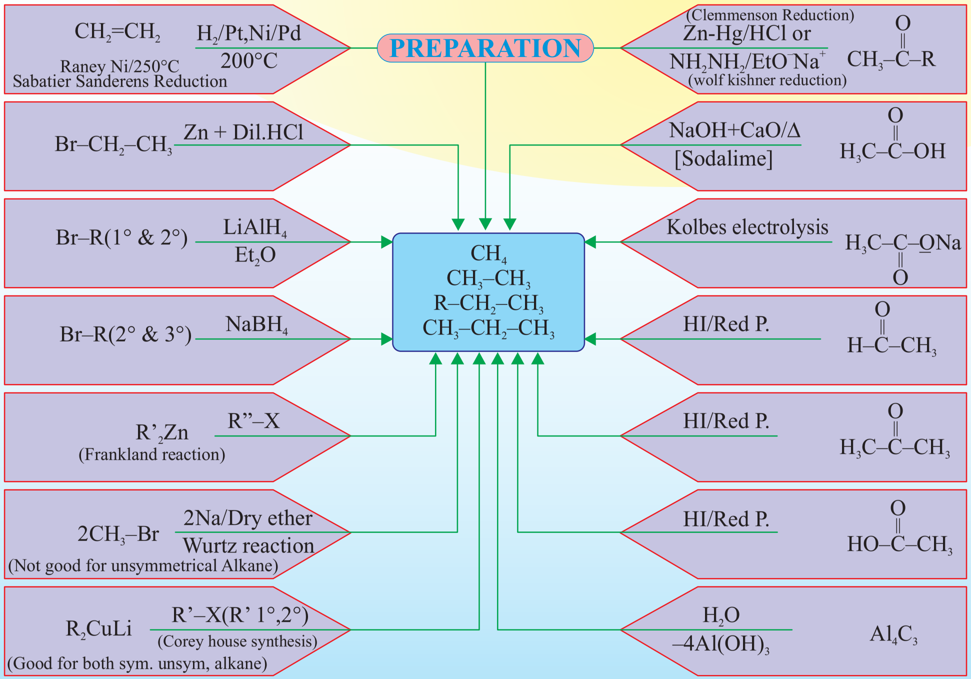
- The order of stability of conformations of n-butane.
  Anti staggered > Gauche > Partially eclipsed > Fully eclipsed.
- Relative stability of various conformation of cyclohexane is Chair > twist boat > boat > half chair.

CHAPTER

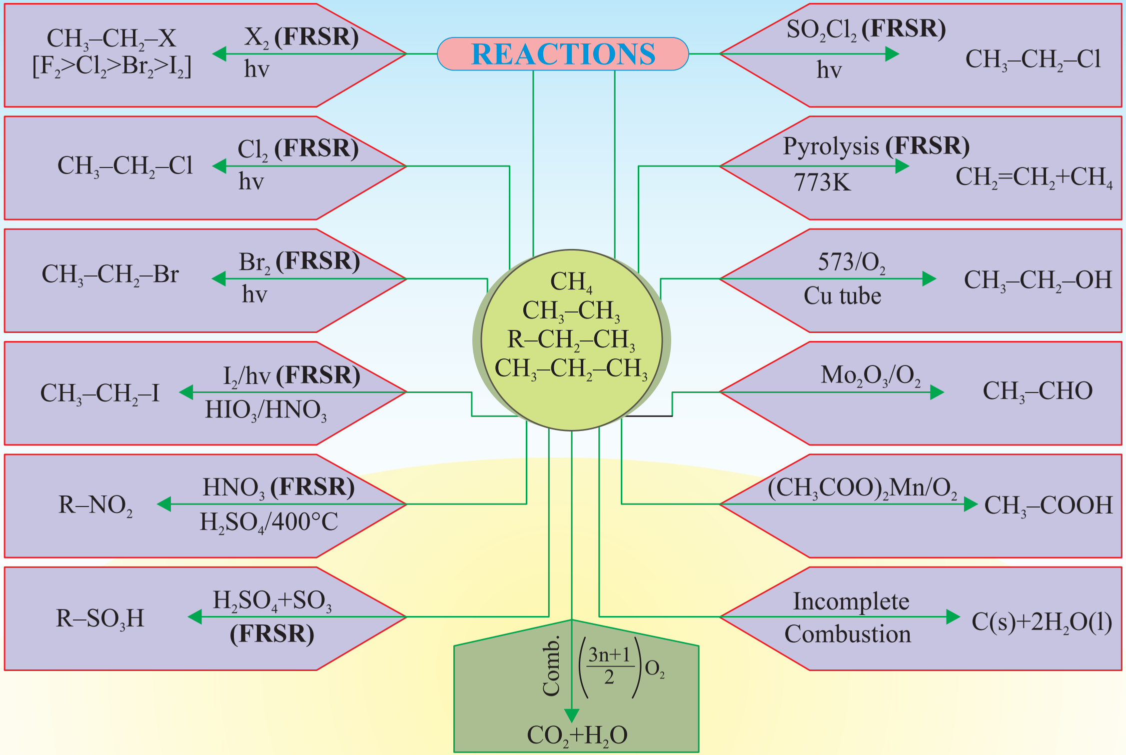
14

Hydrocarbons

ALKANE



HYDROCABON OF ALKANE



REACTIONS

CH_4
CH_3-CH_3
$R-CH_2-CH_3$
$CH_3-CH_2-CH_3$

$\xrightarrow[hv]{X_2\ \textbf{(FRSR)}}$ CH_3-CH_2-X $[F_2>Cl_2>Br_2>I_2]$

$\xrightarrow[hv]{Cl_2\ \textbf{(FRSR)}}$ CH_3-CH_2-Cl

$\xrightarrow[hv]{Br_2\ \textbf{(FRSR)}}$ CH_3-CH_2-Br

$\xrightarrow[HIO_3/HNO_3]{I_2/hv\ \textbf{(FRSR)}}$ CH_3-CH_2-I

$\xrightarrow[H_2SO_4/400°C]{HNO_3\ \textbf{(FRSR)}}$ $R-NO_2$

$\xrightarrow[\textbf{(FRSR)}]{H_2SO_4+SO_3}$ $R-SO_3H$

$\xrightarrow[hv]{SO_2Cl_2\ \textbf{(FRSR)}}$ CH_3-CH_2-Cl

$\xrightarrow[773K]{Pyrolysis\ \textbf{(FRSR)}}$ $CH_2=CH_2+CH_4$

$\xrightarrow[Cu\ tube]{573/O_2}$ CH_3-CH_2-OH

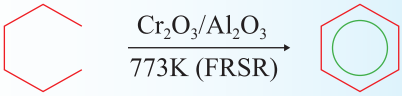
$\xrightarrow{Mo_2O_3/O_2}$ CH_3-CHO

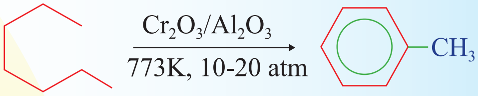
$\xrightarrow{(CH_3COO)_2Mn/O_2}$ CH_3-COOH

$\xrightarrow[Combustion]{Incomplete}$ $C(s)+2H_2O(l)$

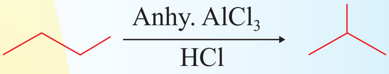
$\xrightarrow[Comb.]{\left(\frac{3n+1}{2}\right)O_2}$ CO_2+H_2O

Aromatization

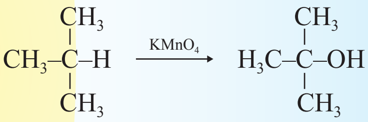




Isomerization



Oxidation at 3°H



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-H \xrightarrow{KMnO_4} H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

- Reactivity of alkane towards free radical halogenation is ∝ stability of free radical

  $C_6H_4{-}CH_3 > CH_2{=}CH{-}CH_3 > (CH_3)_3CH > CH_3{-}CH_2{-}CH_3 > CH_3{-}CH_3 > CH_4$

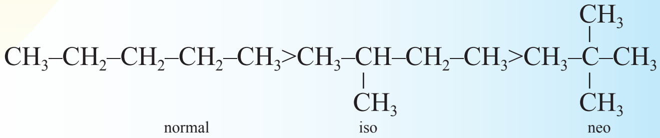
- Reactivity of halogen towards free radical substitution

  $F_2 > Cl_2 > Br_2 > I_2$

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

  Olefin > cycloalkane > aromatic

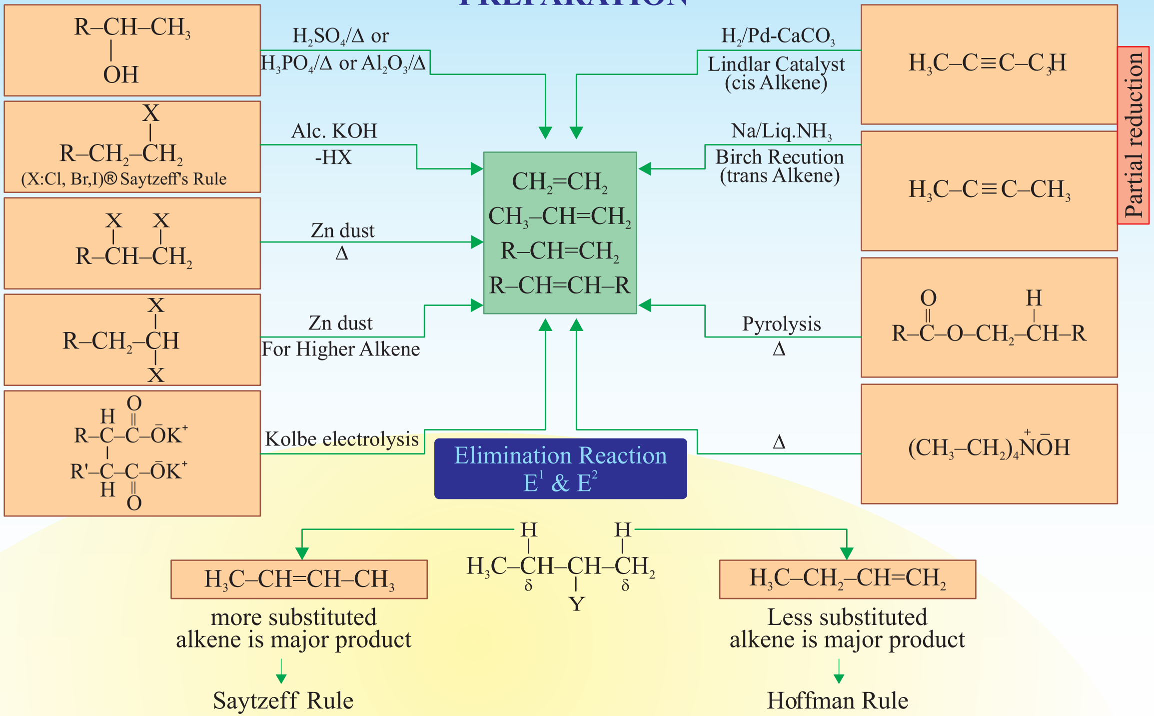
- Boiling point decrease with increase in number of side chain.

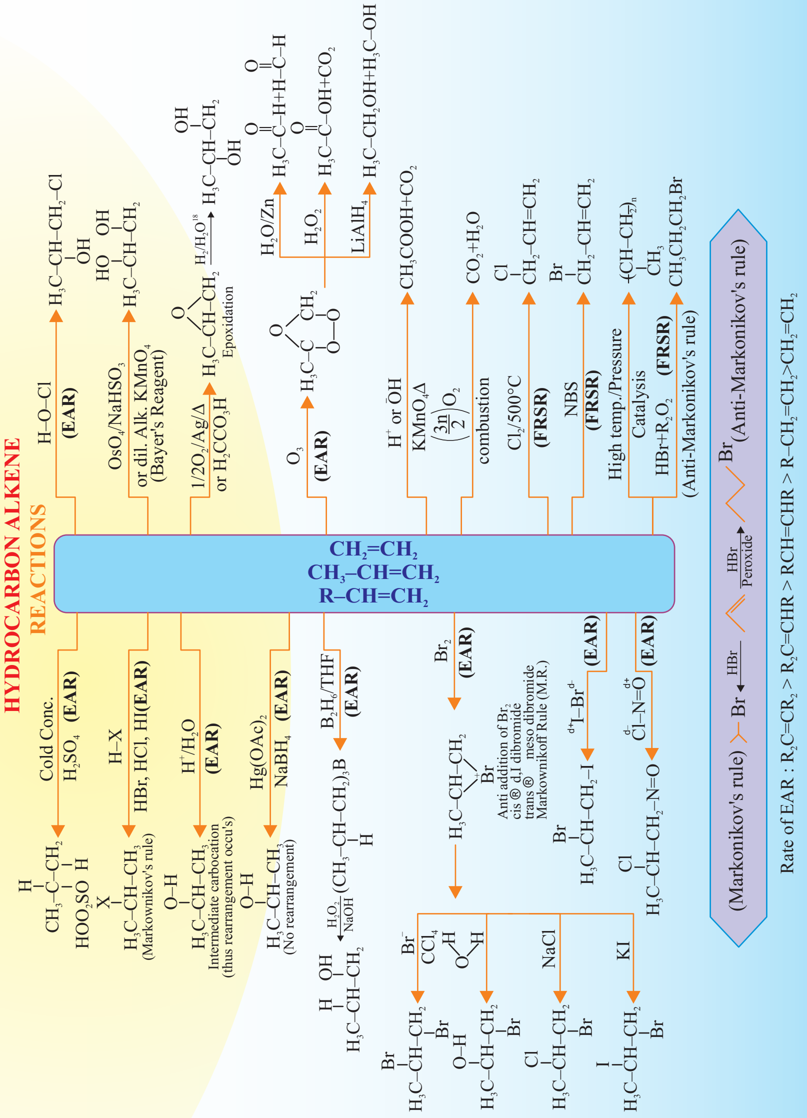


$$\underset{\text{normal}}{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3} > \underset{\text{iso}}{CH_3{-}\underset{CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_3} > \underset{\text{neo}}{CH_3{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}CH_3}$$

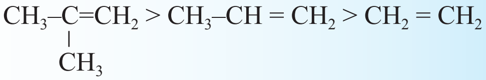
HYDROCARBON–ALKENE

PREPARATION

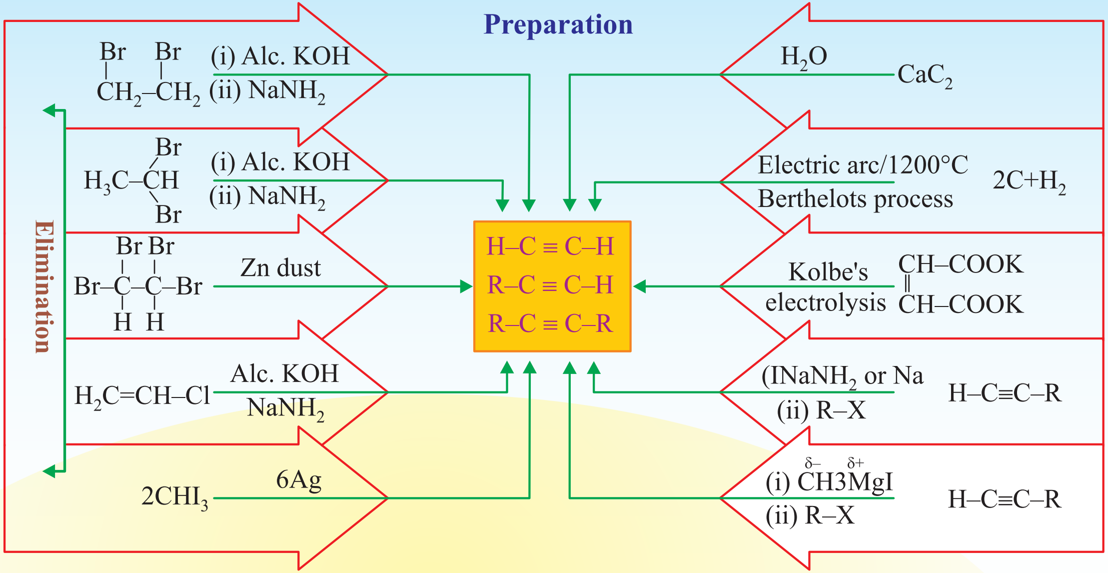




- Order of reactivity of olefins for hydrogenation $CH_2 = CH_2 > R–CH=CH_2$ (Reverse of stability)
- Order of reactivity of alkene towards hydration

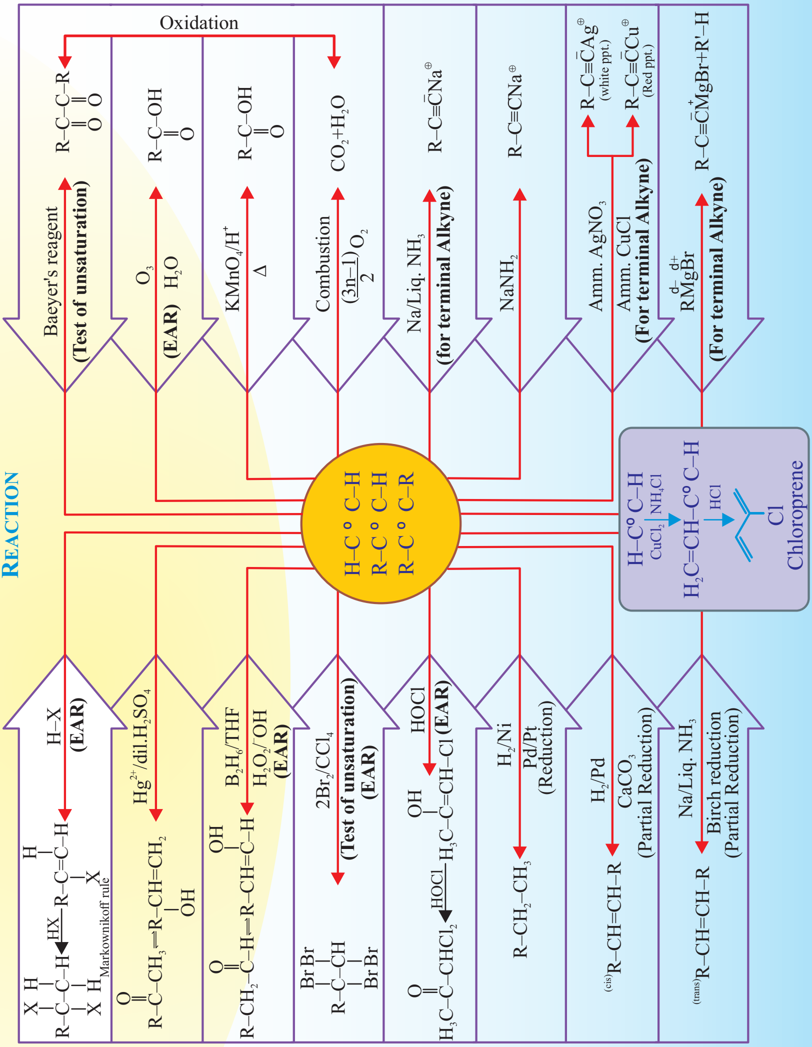


$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 > CH_3-CH = CH_2 > CH_2 = CH_2$$

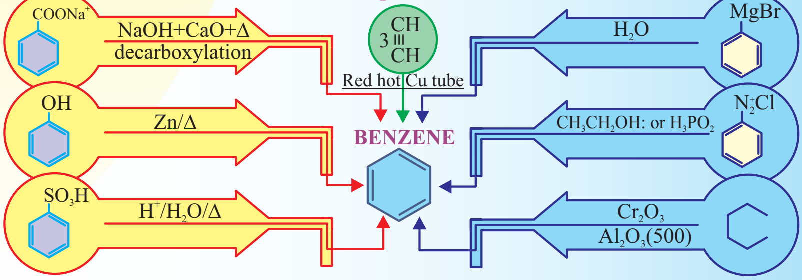

Preparation
Elimination
H–C ≡ C–H
R–C ≡ C–H
R–C ≡ C–R
Br Br
CH₂–CH₂
(i) Alc. KOH
(ii) NaNH₂
Br
H₃C–CH
Br
(i) Alc. KOH
(ii) NaNH₂
Br Br
Br–C–C–Br
H H
Zn dust
H₂C=CH–Cl
Alc. KOH
NaNH₂
2CHI₃
6Ag
H₂O
CaC₂
Electric arc/1200°C
Berthelots process
2C+H₂
Kolbe's
electrolysis
CH–COOK
CH–COOK
(INaNH₂ or Na
(ii) R–X
H–C≡C–R
δ– δ+
(i) CH3MgI
(ii) R–X
H–C≡C–R

HYDROCABON-ALKYNE

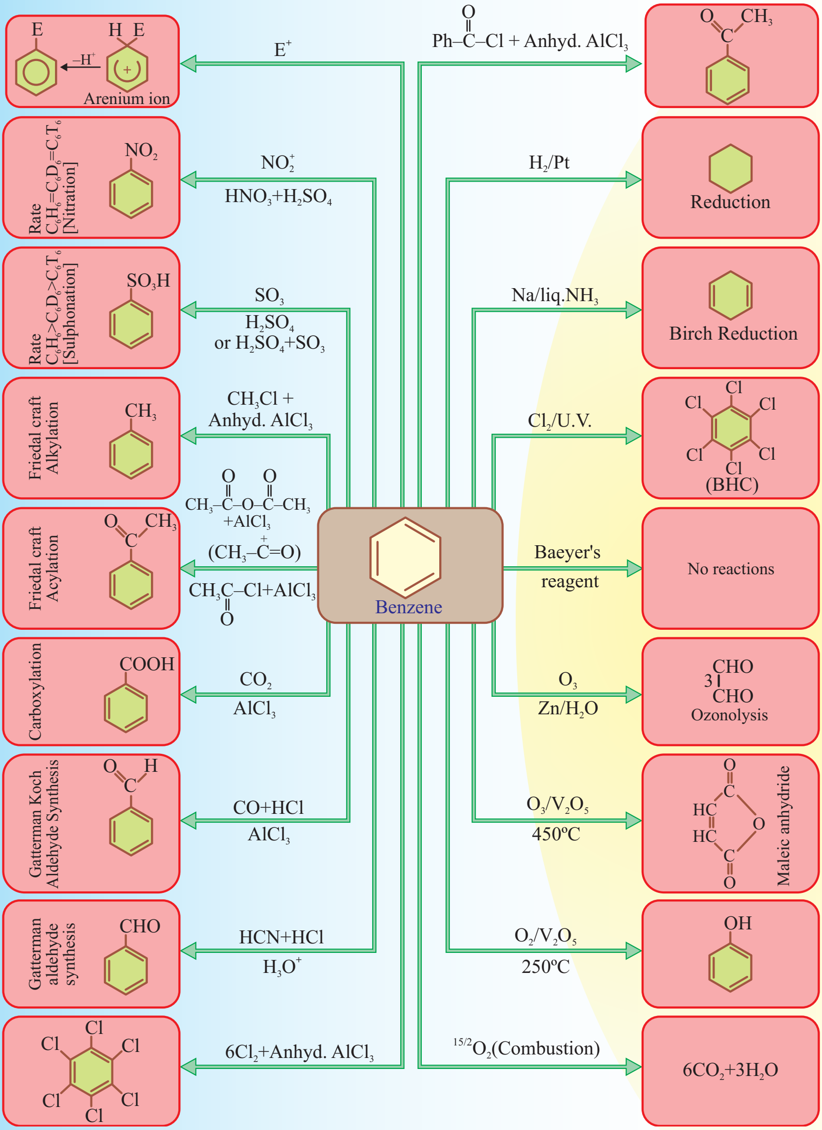
REACTION



Preparation



Reaction
Electrophilic Substitution Reactions



CHAPTER 15

Environment Pollution

POLLUTANT

Substance which cause pollution is known as pollutant.

Atmospheric pollution → Tropospheric pollution
Atmospheric pollution → Stratospheric pollution

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

Gaseous Pollutant

SO_2: Cause respiratory diseases of anthma, bronchitis emphysema etc & irrataling to eyes.

NO_2: Form by fossil fuel burn, Damage lungs.

Higer concentration of NO_2 damage the leaves of plant and retard rate of photosynthesis.

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

Oxide of Carbon

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

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

CO_2: Main source is respiration, burning of fossil fuels, demposition of lime stone in cement industry.

Increase of CO_2 cause global warming.

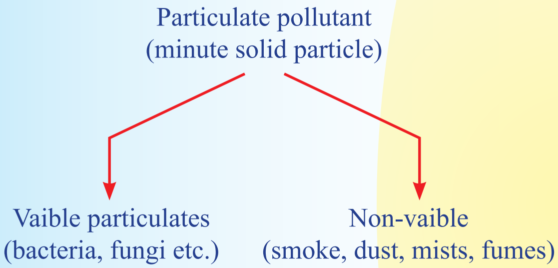
Global WWarming and Green House Effect

Some of the gases such as CO_2, CH_4,O_3 CFC(s) and water vapour tapped 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 than 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 1µm diameter, produced by crushin, grinding etc.

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

NOTES

Pb is major air pollutant.

Smog (Smoke + Fog)

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

Photochemical smog:

$$\text{hydrocarbon : NO} \xrightarrow{hv}$$

$$NO_2 \xrightarrow{hv} NO + O$$

$$O + O_2 \xrightarrow{hv} O_3$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

→ contribute of Haze

$(NO_2 + O_2)$ + hydrocarbon

→ CH_2O
formaldelyde
or
$CH_2 = CHCHO$
A.crotein
or
CH_3COONO_2
peroxy acetyl nitrate (PAN)

Stratospheric Pollution

Formation & decomposition of ozone.

$$O_2(g) \xrightarrow{UV} O(g) + O(g)$$

$$O_2(g) + O(g) \xrightleftharpoons{UV} O_3$$

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

$$CF_2Cl_2(g) \xrightarrow{UV} \dot{C}l(g) + \dot{C}F_2Cl(g)$$

$$\dot{C}l(g) + O_3(g) \longrightarrow \dot{C}lO(g) + O_2(g)$$

$$\dot{C}lO(g) + NO_2(g) \longrightarrow \dot{C}lONO_2(g)$$

$$\dot{C}l(g) + CH_4(g) \longrightarrow \dot{C}H_3(g) + HCl(g)$$

$$ClONO_2(g) + H_2O(g) \longrightarrow HOCl(g) + HNO_3(g)$$

$$ClONO_2(g) + HCl(g) \longrightarrow Cl(g) + HNO_3(g)$$

$$HOCl \xrightarrow{hv} \dot{O}H(g) + \dot{C}l(g)$$

$$Cl_2(g) \longrightarrow 2\dot{C}l(g)$$

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

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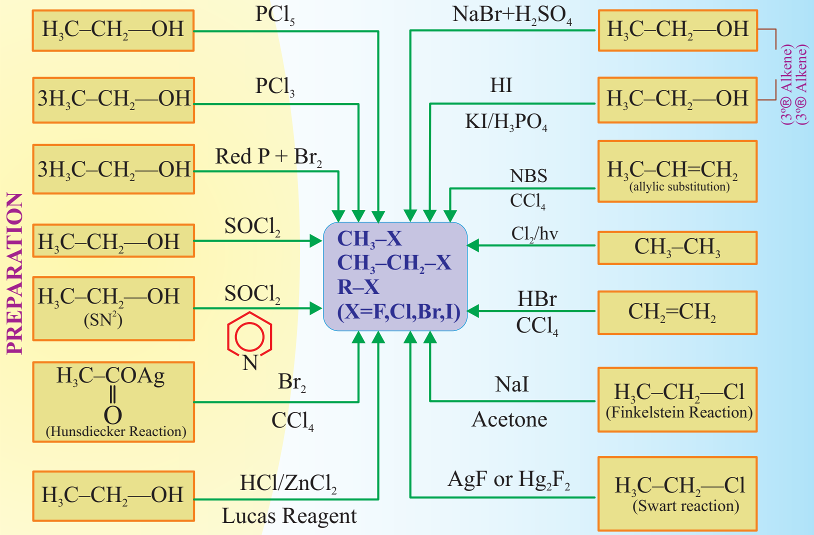
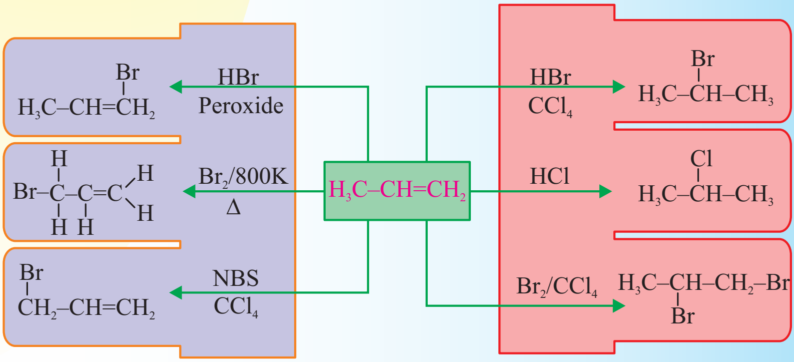
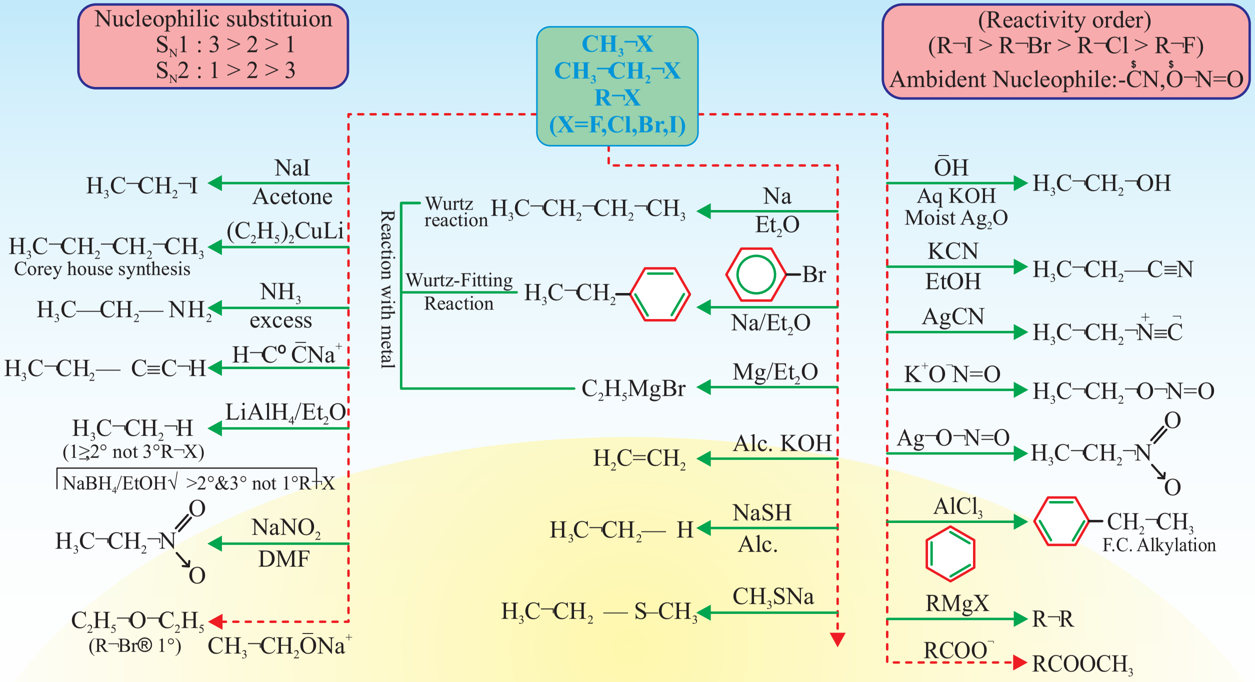
CHAPTER 16

Haloalkane and Haloarene





REACTIONS

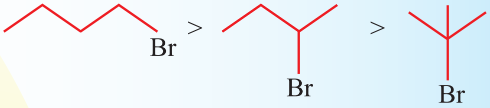

Nucleophilic substituion
$S_N1 : 3 > 2 > 1$
$S_N2 : 1 > 2 > 3$
CH_3-X
CH_3-CH_2-X
$R-X$
$(X=F,Cl,Br,I)$
(Reactivity order)
$(R-I > R-Br > R-Cl > R-F)$
Ambident Nucleophile:-$\overset{\$}{C}N$,$\overset{\$}{O}-N=O$
NaI
Acetone
H_3C-CH_2-I
$(C_2H_5)_2CuLi$
$H_3C-CH_2-CH_2-CH_3$
Corey house synthesis
NH_3
excess
$H_3C-CH_2-NH_2$
$H-C^o\bar{C}Na^+$
$H_3C-CH_2-C\equiv C-H$
$LiAlH_4/Et_2O$
H_3C-CH_2-H
(1≥2° not 3°R–X)
$NaBH_4$/EtOH√ >2°&3° not 1°R–X
$NaNO_2$
DMF
$H_3C-CH_2-N(=O)\to O$
$CH_3-CH_2\bar{O}Na^+$
$C_2H_5-O-C_2H_5$
(R–Br® 1°)
Reaction with metal
Na
Et_2O
Wurtz reaction
$H_3C-CH_2-CH_2-CH_3$
Br
Na/Et_2O
Wurtz-Fitting Reaction
H_3C-CH_2-
Mg/Et_2O
C_2H_5MgBr
Alc. KOH
$H_2C=CH_2$
NaSH
Alc.
H_3C-CH_2-H
CH_3SNa
$H_3C-CH_2-S-CH_3$
$\bar{O}H$
Aq KOH
Moist Ag_2O
H_3C-CH_2-OH
KCN
EtOH
$H_3C-CH_2-C\equiv N$
AgCN
$H_3C-CH_2-\overset{+}{N}\equiv\overset{-}{C}$
$K^+O^-N=O$
$H_3C-CH_2-O-N=O$
$Ag-O-N=O$
$H_3C-CH_2-N(=O)\to O$
$AlCl_3$
CH_2-CH_3
F.C. Alkylation
RMgX
R–R
$RCOO^-$
$RCOOCH_3$

Physical Properties

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

(2) Bond enthalpies: $CH_3–F > CH_3–Cl > CH_3–Br > CH_3–I$

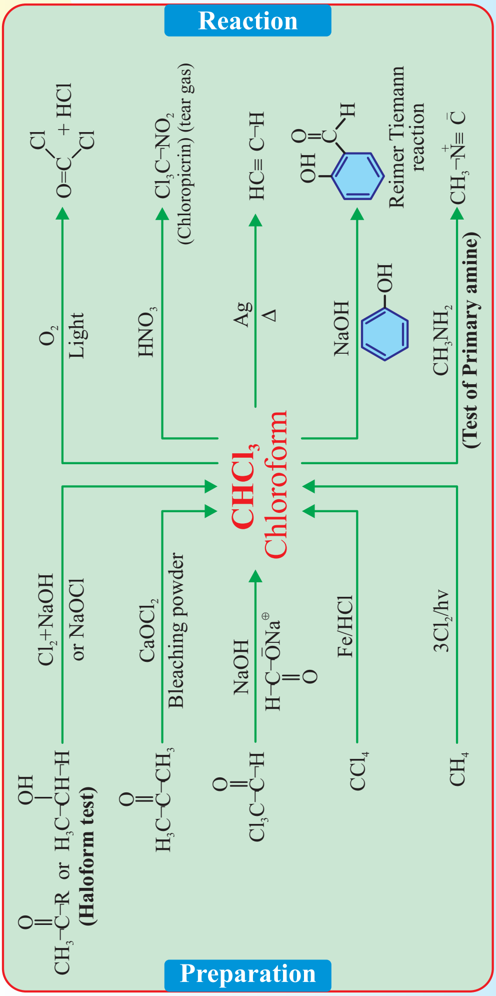
(3) Boiling point: R–I > R–Br > R–Cl > R–F

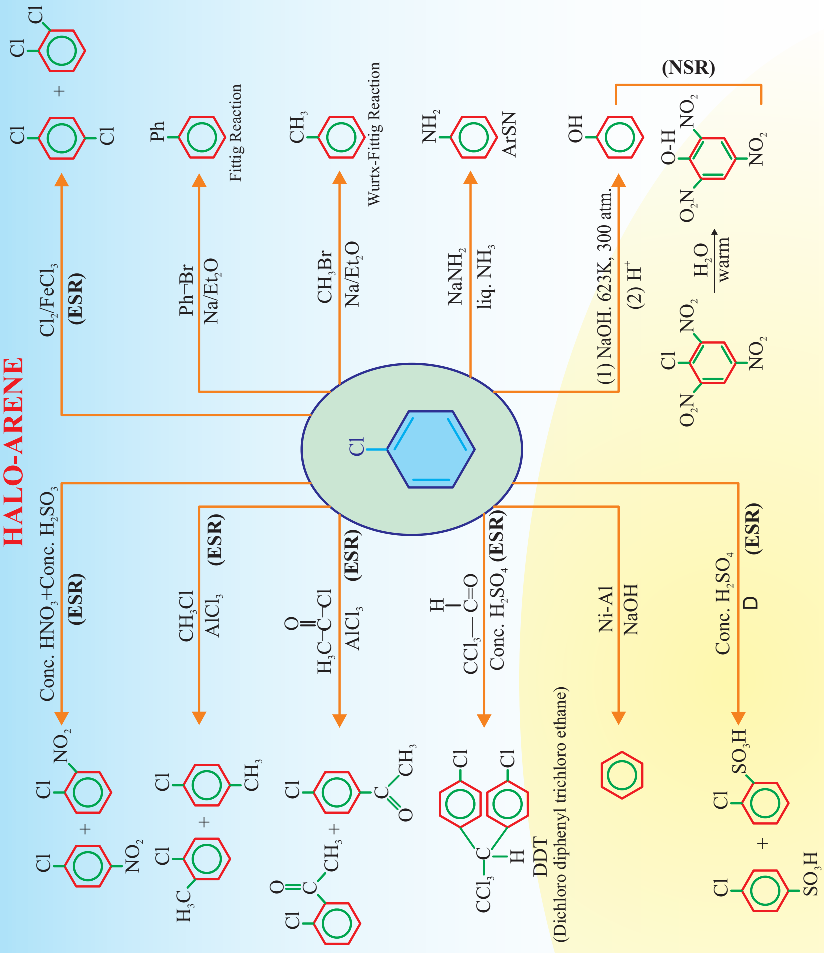


(4) Density: $n–C_3H_7Cl < n–C_3H_7Br < n–C_3H_7I$

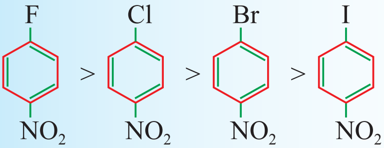
(5) Solubility → slightly soluble in water

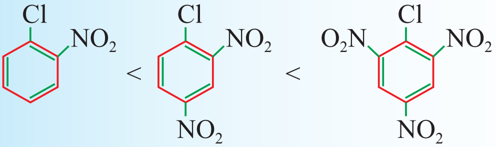
TRI-HALO ALKANE



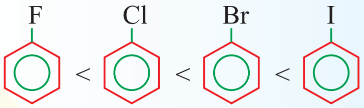


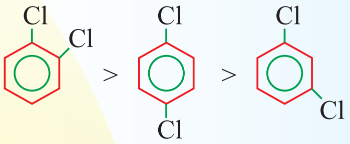
(A) [Reactivity toward Nucleophile]

(i) 

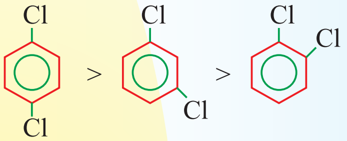
(ii) 

(B) Boiling point

(i) 

(ii) 

(C) Melting point

(i) 

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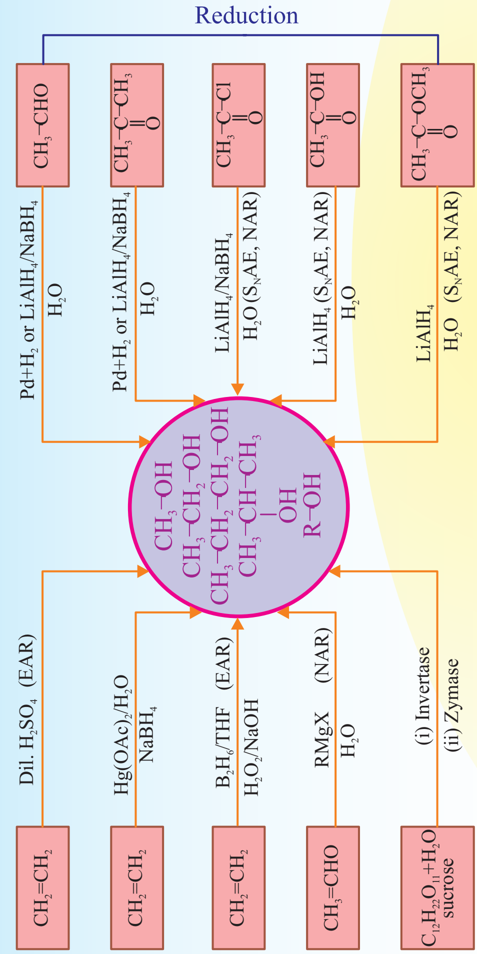
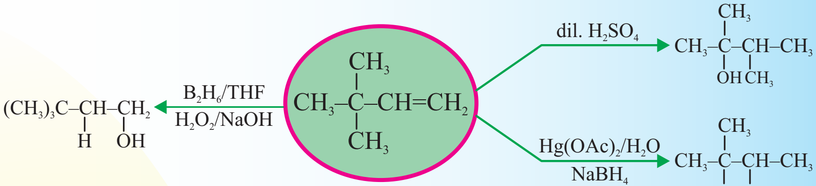
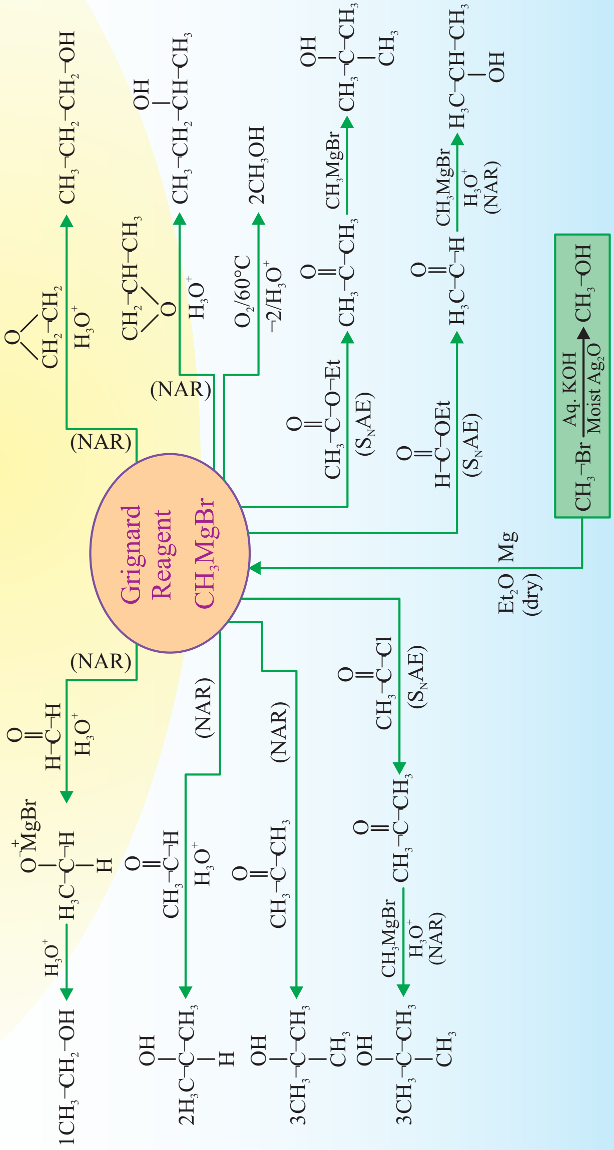
CHAPTER

17

Alcohols, Phenols and Ethers




CH3–C(CH3)2–CH=CH2
B2H6/THF
H2O2/NaOH
(CH3)3C–CH–CH2 (H, OH)
dil. H2SO4
CH3–C(CH3)(OH)–CH(CH3)–CH3
Hg(OAc)2/H2O
NaBH4
CH3–C(CH3)(CH3)–CH(OH)–CH3


Grignard Reagent CH3MgBr
CH3–Br → CH3–OH (Aq. KOH / Moist Ag2O)
Mg, Et2O (dry)
(NAR)
epoxide CH2–CH2 (O), H3O+ → CH3–CH2–CH2–OH
CH2–CH–CH3 (O), H3O+ → CH3–CH2–CH(OH)–CH3
O2/60°C, –2/H3O+ → 2CH3OH
CH3–C(=O)–O–Et (SNAE) → CH3–C(=O)–CH3, CH3MgBr → CH3–C(OH)(CH3)–CH3
H–C(=O)–OEt (SNAE) → H3C–C(=O)–H, CH3MgBr, H3O+ (NAR) → H3C–CH(OH)–CH3
H–C(=O)–H, H3O+ → H3C–C(O–MgBr+)(H)–H, H3O+ → 1CH3–CH2–OH
CH3–C(=O)–H, H3O+ → 2H3C–C(OH)(CH3)–H
CH3–C(=O)–CH3 → 3CH3–C(OH)(CH3)–CH3
CH3–C(=O)–Cl (SNAE) → CH3–C(=O)–CH3, CH3MgBr, H3O+ (NAR) → 3CH3–C(OH)(CH3)–CH3

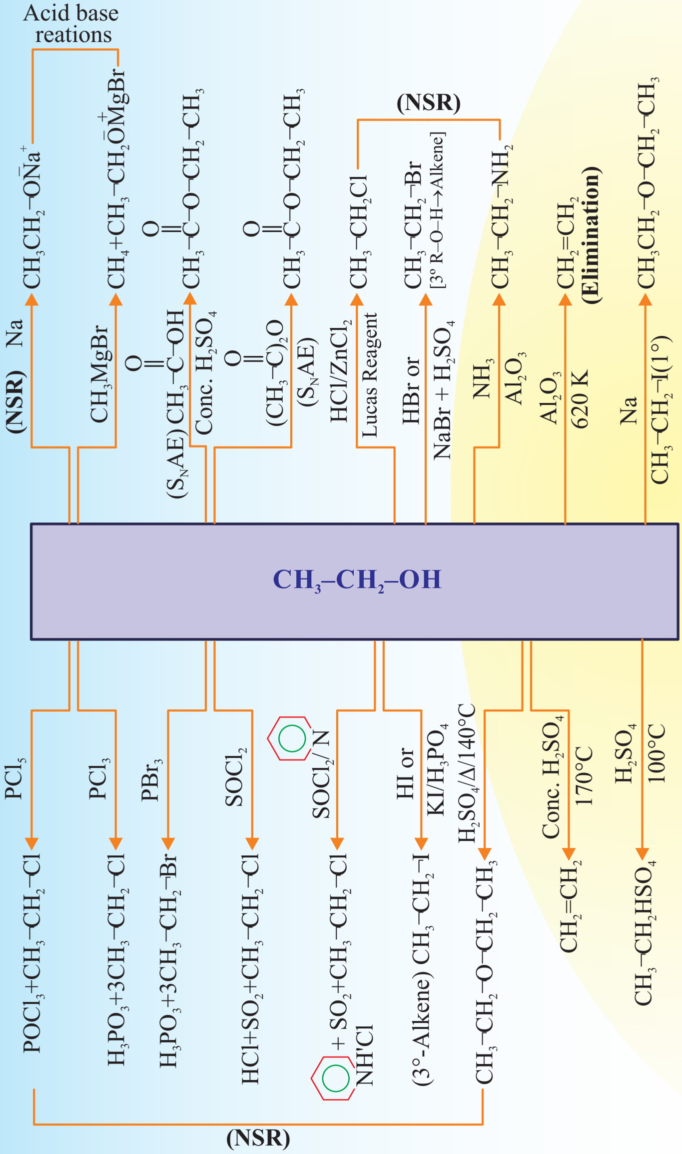
Solubility of alcohol increase in branching n < iso < neo (Isomeric).

Relative order of reactivity

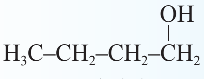
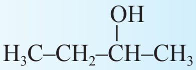
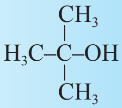
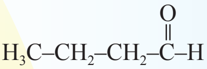
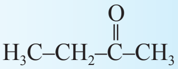
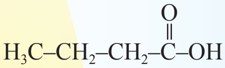
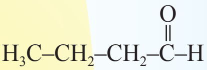
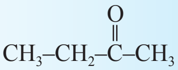
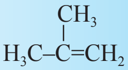
(i) 1° > 2° > 3° (O–H bond fission)

(ii) 3° > 2° > 1° > (C–O bond fission)

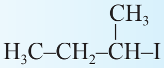
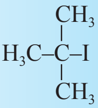
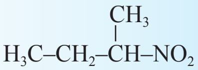
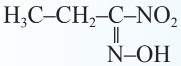
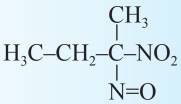
(iii) 3° > 2° > 1° (Dehydration)

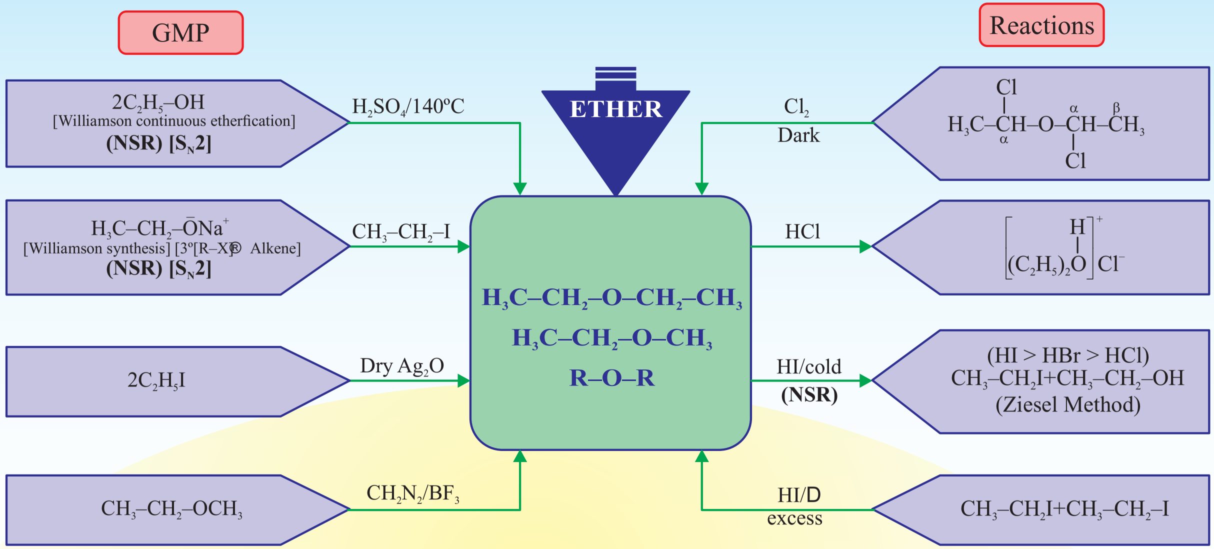


DEHYDROGENATIONS

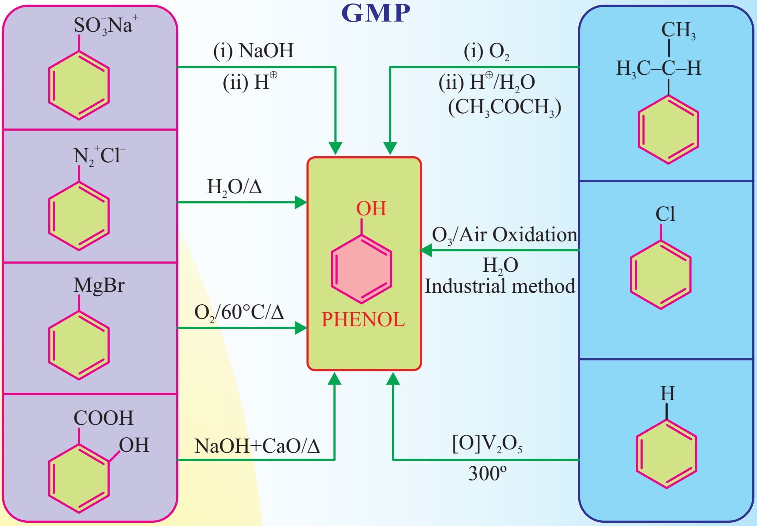
Reagent	 $H_3C{-}CH_2{-}CH_2{-}\overset{\overset{OH}{\vert}}{CH_2}$ 1° Alcohol	 $H_3C{-}CH_2{-}\overset{\overset{OH}{\vert}}{CH}{-}CH_3$ 2°Alcohol	 $H_3C{-}\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}{-}OH$ 3° Alcohol
PCC/PDC Anhy. CrO_3	 $H_3C{-}CH_2{-}CH_2{-}\overset{\overset{O}{\Vert}}{C}{-}H$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

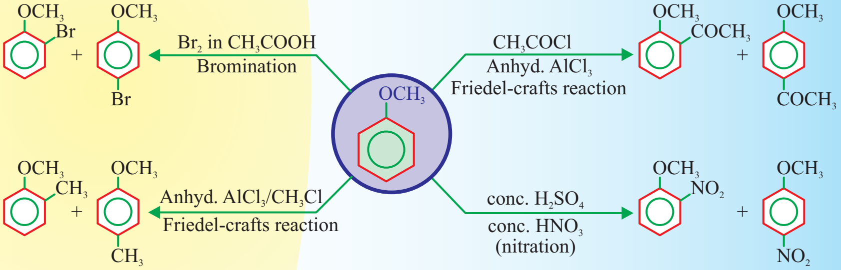
VICTOR MEYER'S TEST

P/I_2	$CH_3{-}CH_2{-}CH_2{-}CH_2{-}I$	 $H_3C{-}CH_2{-}\overset{\overset{CH_3}{\vert}}{CH}{-}I$	 $H_3C{-}\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}{-}I$
$AgNO_2$	$CH_3{-}CH_2{-}CH_2{-}NO_2$	 $H_3C{-}CH_2{-}\overset{\overset{CH_3}{\vert}}{CH}{-}NO_2$	$(CH_3)_3C{-}NO_2$
HNO_2	 $H_3C{-}CH_2{-}\underset{\underset{N-OH}{\Vert}}{C}{-}NO_2$ Nitrolic acid	 $H_3C{-}CH_2{-}\overset{\overset{CH_3}{\vert}}{\underset{\underset{N=O}{\vert}}{C}}{-}NO_2$ Blue colour	No reaction: Colourless
NaOH	Red Colour	No reaction	

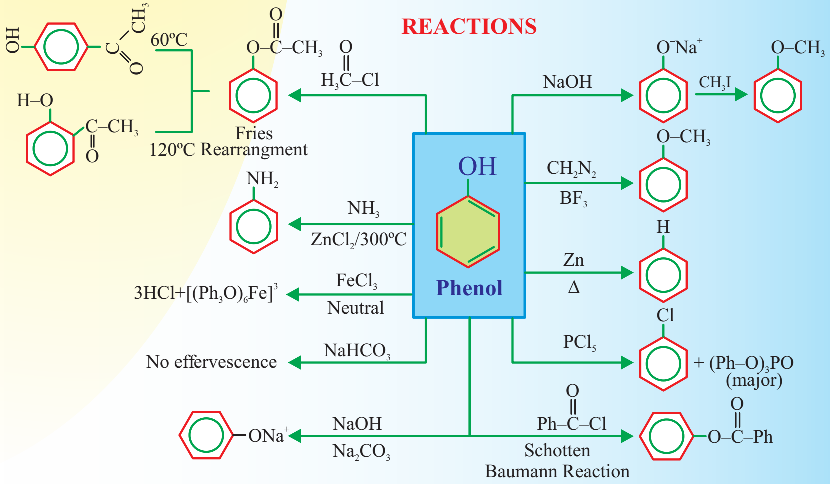

GMP
Reactions
ETHER
$H_3C-CH_2-O-CH_2-CH_3$
$H_3C-CH_2-O-CH_3$
R–O–R
$2C_2H_5-OH$
[Williamson continuous etherfication]
(NSR) [S_N2]
$H_2SO_4/140°C$
$H_3C-CH_2-\bar{O}Na^+$
[Williamson synthesis] [3°[R–X® Alkene]
(NSR) [S_N2]
CH_3-CH_2-I
$2C_2H_5I$
Dry Ag_2O
$CH_3-CH_2-OCH_3$
CH_2N_2/BF_3
Cl_2
Dark
Cl, Cl, α, α, β
$H_3C-CH-O-CH-CH_3$
HCl
$\left[(C_2H_5)_2\overset{H}{O}\right]^+Cl^-$
HI/cold
(NSR)
(HI > HBr > HCl)
$CH_3-CH_2I+CH_3-CH_2-OH$
(Ziesel Method)
HI/D
excess
$CH_3-CH_2I+CH_3-CH_2-I$

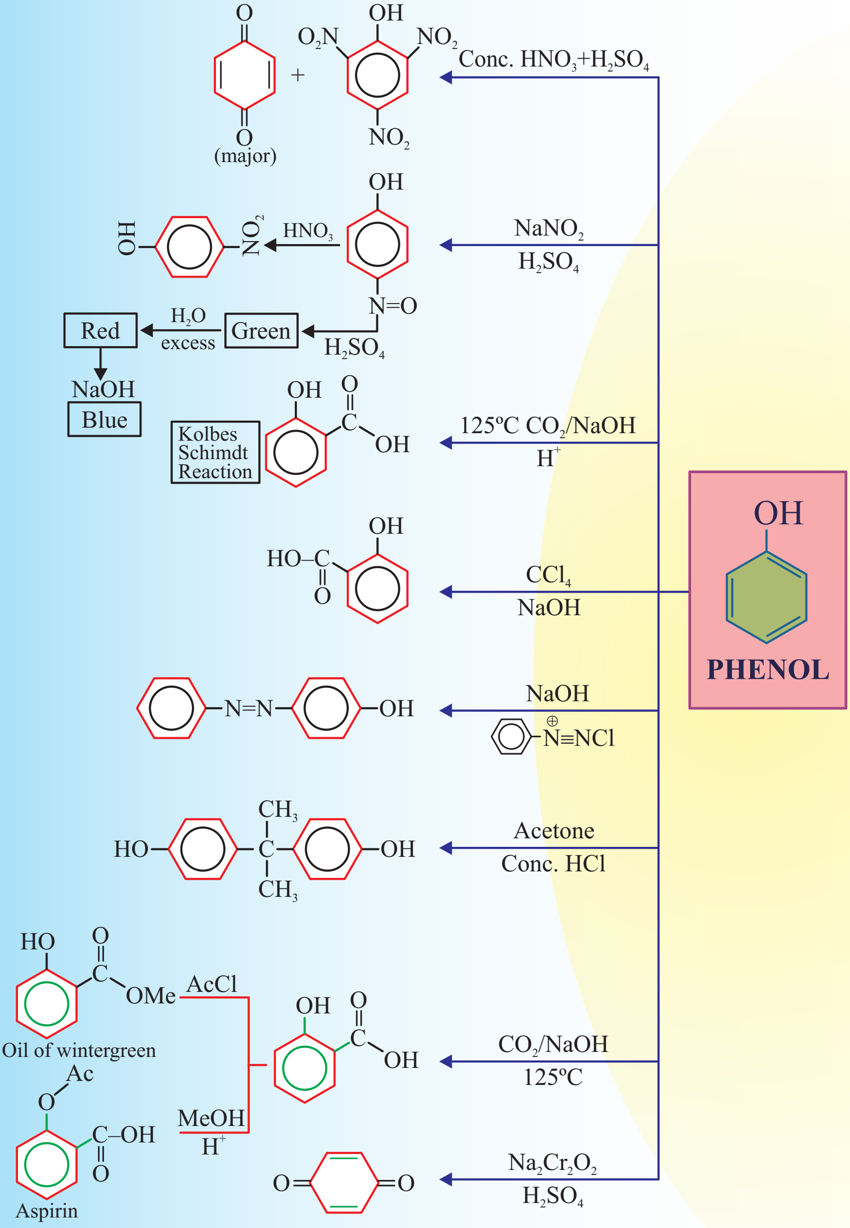
PHENOL
GMP

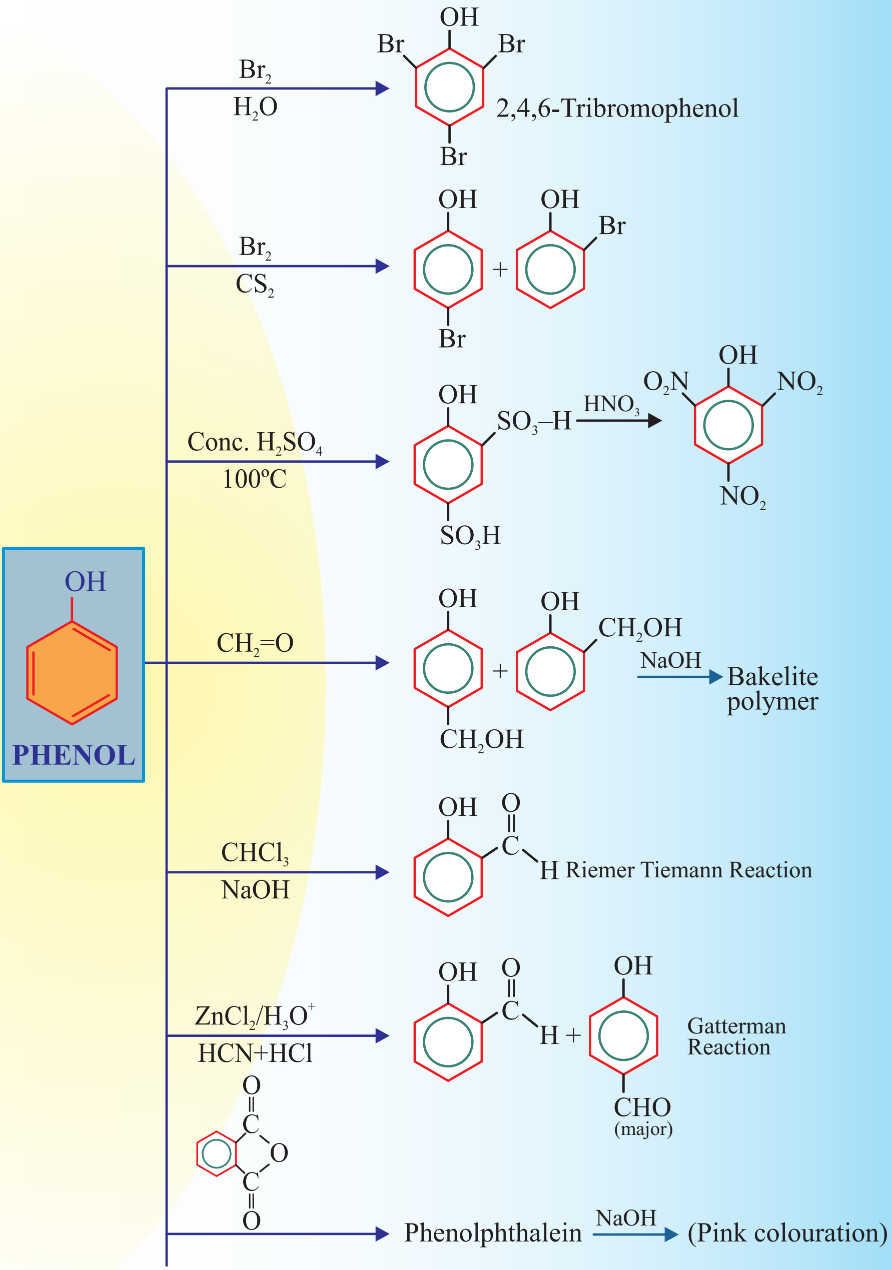




REACTIONS




PHENOL
OH
Conc. HNO$_3$+H$_2$SO$_4$
O
O
(major)
+
O$_2$N
NO$_2$
NO$_2$
OH
NaNO$_2$
H$_2$SO$_4$
N=O
HNO$_3$
NO$_2$
OH
H$_2$SO$_4$
Green
H$_2$O
excess
Red
NaOH
Blue
125ºC CO$_2$/NaOH
H$^+$
Kolbes Schimdt Reaction
OH
C
OH
O
CCl$_4$
NaOH
HO–C
O
OH
NaOH
N≡NCl
⊕
N=N
OH
Acetone
Conc. HCl
HO
CH$_3$
C
CH$_3$
OH
CO$_2$/NaOH
125ºC
OH
C
OH
O
AcCl
MeOH
H$^+$
HO
C
OMe
O
Oil of wintergreen
Ac
O
C–OH
O
Aspirin
Na$_2$Cr$_2$O$_2$
H$_2$SO$_4$
O=
=O


PHENOL
OH
Br2
H2O
OH
Br
Br
Br
2,4,6-Tribromophenol
Br2
CS2
OH
Br
+
OH
Br
Conc. H2SO4
100ºC
OH
SO3–H
SO3H
HNO3
OH
O2N
NO2
NO2
CH2=O
OH
CH2OH
+
OH
CH2OH
NaOH
Bakelite polymer
CHCl3
NaOH
OH
O
C
H Riemer Tiemann Reaction
ZnCl2/H3O+
HCN+HCl
OH
O
C
H +
OH
CHO
(major)
Gatterman Reaction
O
C
O
C
O
Phenolphthalein
NaOH
(Pink colouration)

Comparison of S_N1 and S_N2

Reactions		S_N1	S_N2
A	Kinetics	1^{st} order	2^{nd} order
B	Rate	k[RX]	k[RX] $[Nu:^{\ominus}]$
C	Stereochemistry	Racemisation	Inversion
D	Substrate (reactivity)	$3^\circ > 2^\circ > 1^\circ > MeX$	$MeX > 1^\circ > 2^\circ > 3^\circ$
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	$3^\circ > 2^\circ >>> 1^\circ$	$3^\circ > 2^\circ > 1^\circ$
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_N1, S_N2, E_1 and E_2 Reactions

RX	Mechanism	$\overset{\ominus}{Nu}/\overset{\ominus}{B}$	Solvent	Temp.
1°	S_N2	Better $\overset{\ominus}{O}H, C_2H_5\overset{\ominus}{O}$	Polar aprotic	Low
	E_2	Strong & bulky base $(CH_3)_3C\overset{\ominus}{O}$		High
2°	S_N2	$H\overset{\ominus}{O}; C_2H_5\overset{\ominus}{O}$	Polar aprotic	Low
	E_2	$(CH_3)_3C\overset{\ominus}{O}$		High
	(S_N1)	(Solvent)	Polar protic	(Low)
	(E_1)	(Solvent)		(High)
3°	S_N1	Solvent	Protic	Low
	E_1	Solvent	Protic	High

	Primary (1º)	**Secondary (2º)**	**Tertiary (3º)**
Strong nucleophile	$S_N2 >> E_2$	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

$S_N1 \propto$ Benzylic > Allylic > 3º > 2º > 1º

$S_N1 \propto$ Stability of carbocation

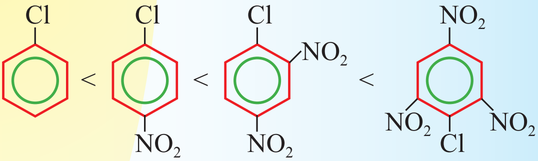
$S_N2 \propto 1º > 2º > 3º$

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

Reactivity order towards S_N1 or S_N2 and E_1 or E_2

R–I > R–Br > R–Cl > R–F

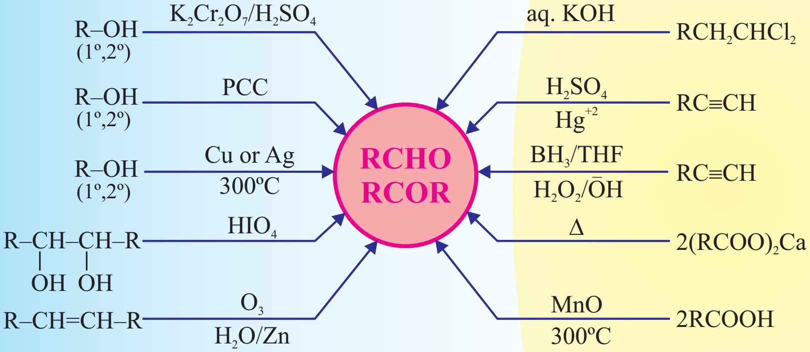
With increase in number of strong electron withdrawing group at ortho and para position, reactivity of X towards aromatic nucleophilic substitution increases.



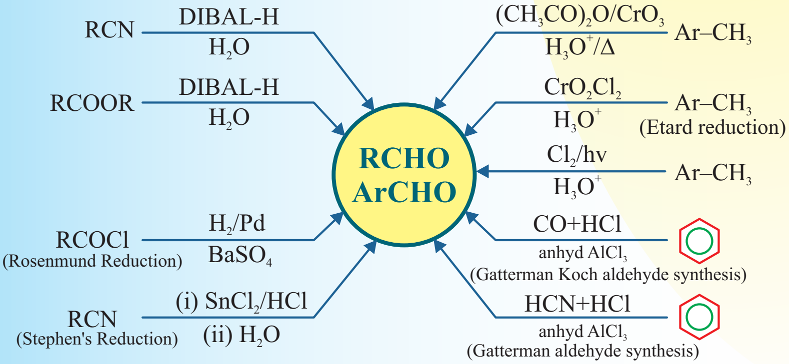
CHAPTER 18

Aldehydes, Ketones and Carboxylic Acids

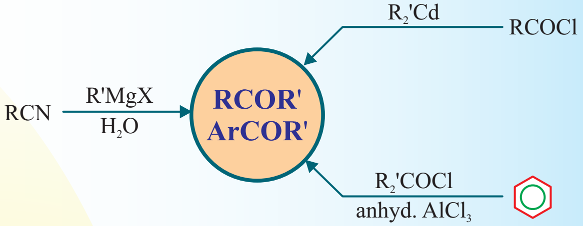
Preparation of Aldehyde & Ketone both



Preparation of Aldehyde only

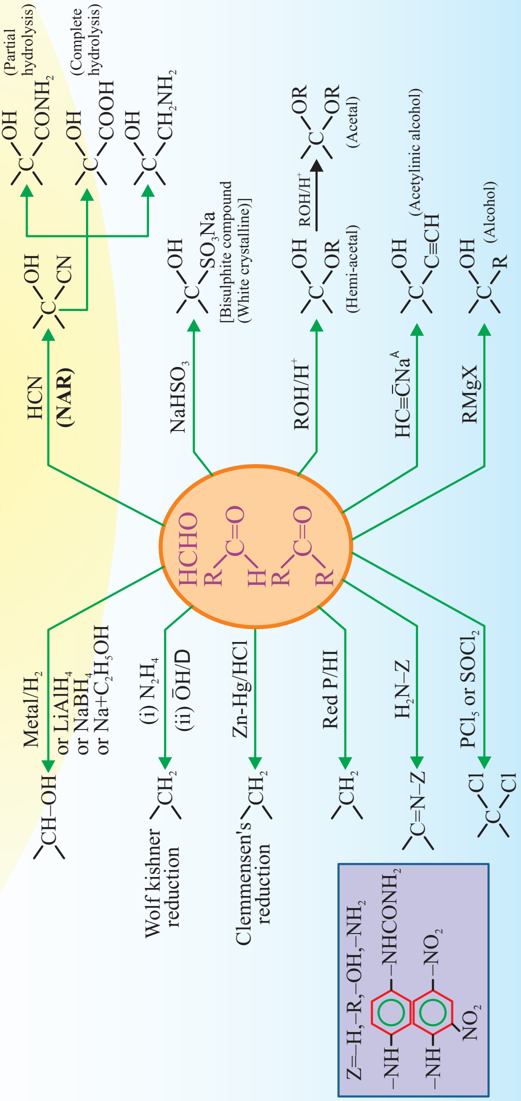


Preparation of Ketone only

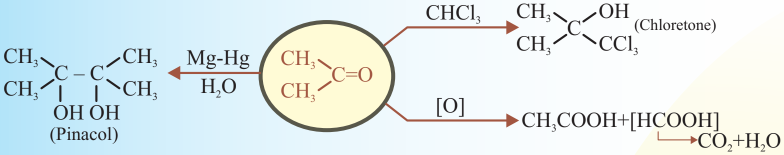


ALDEHYDE & KETONE

Reaction of Aldehyde & Ketone

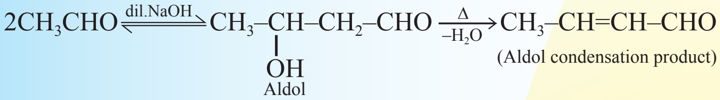


Reaction of only Ketone



Aldol Reaction (Aldehyde or ketone with αH)

(i)

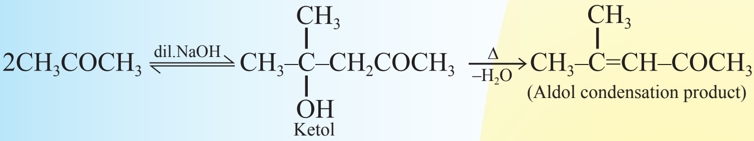


$$2CH_3CHO \overset{\text{dil.NaOH}}{\rightleftharpoons} CH_3-\underset{\substack{|\\ OH}}{CH}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

Aldol

(Aldol condensation product)

(ii)



$$2CH_3COCH_3 \overset{\text{dil.NaOH}}{\rightleftharpoons} CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ OH}}{C}}-CH_2COCH_3 \xrightarrow[-H_2O]{\Delta} CH_3-\overset{\substack{CH_3\\ |}}{C}=CH-COCH_3$$

Ketol

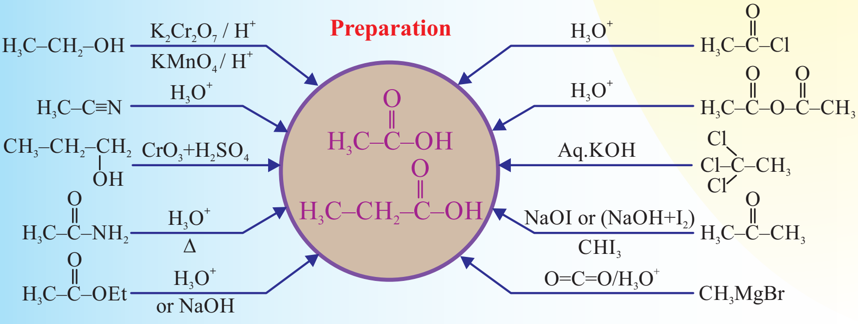
(Aldol condensation product)

Cannizzaro reaction (Aldehyde with no αH)

$$2HCHO \xrightarrow[\Delta]{\text{conc. NaOH}} CH_3OH+HCOO^-Na^+$$

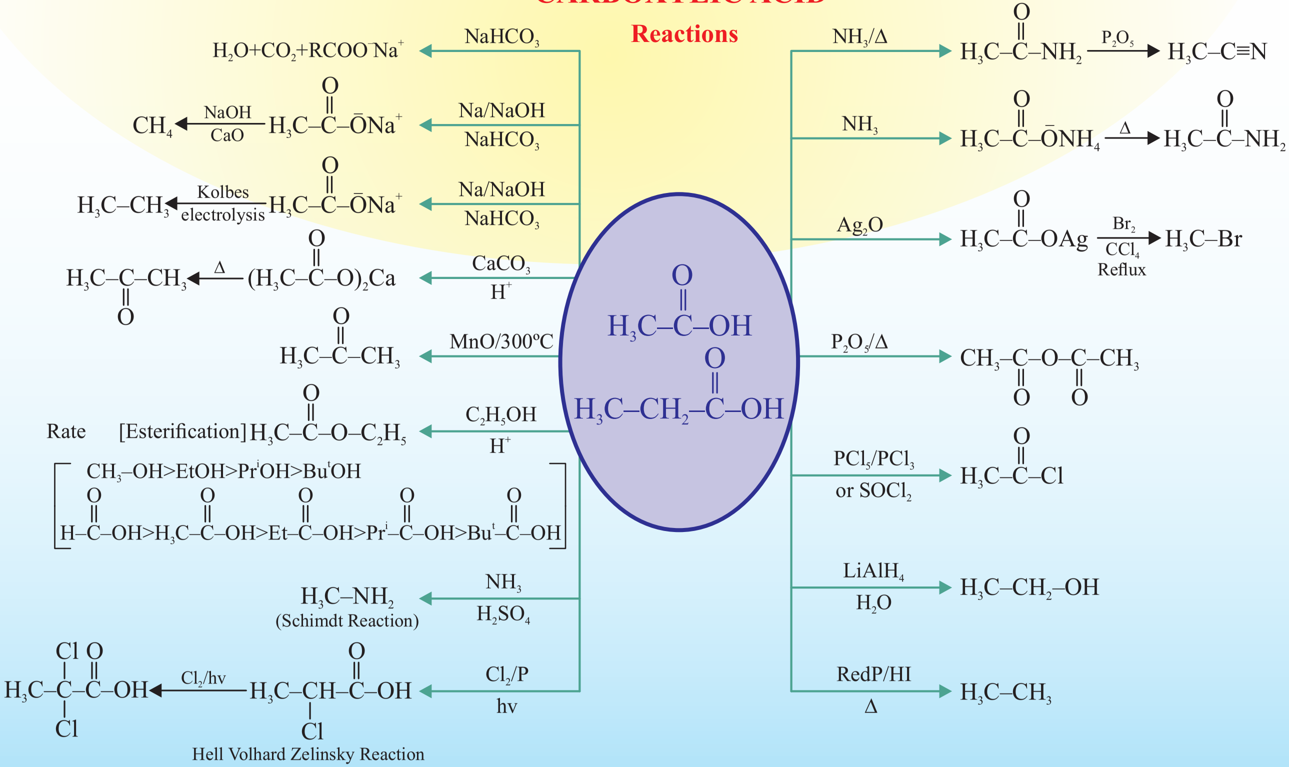
TEST	**Tollen's test** $RCHO+2[Ag(NH_3)_2]^+ + 3^-OH \rightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$ (Given by Aliphatic and aromatic aldehyde)
	Fehling's test $RCHO+2Cu^{+2}+5^-OH \rightarrow RCOO^- + Cu_2O + 3H_2O$ (Given by Aliphatic aldehyde) (Red-Brown ppt.)

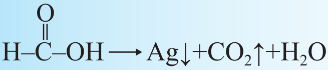
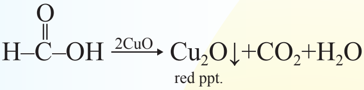
Preparation

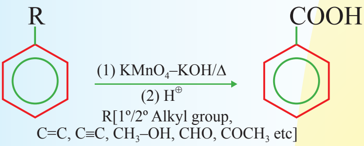


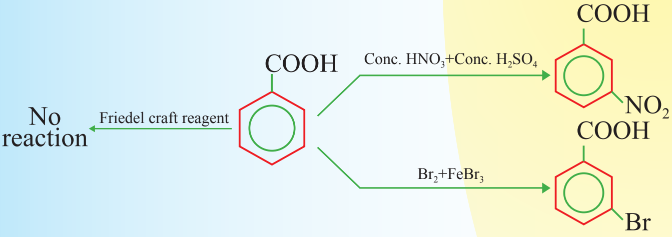
CARBOXYLIC ACID

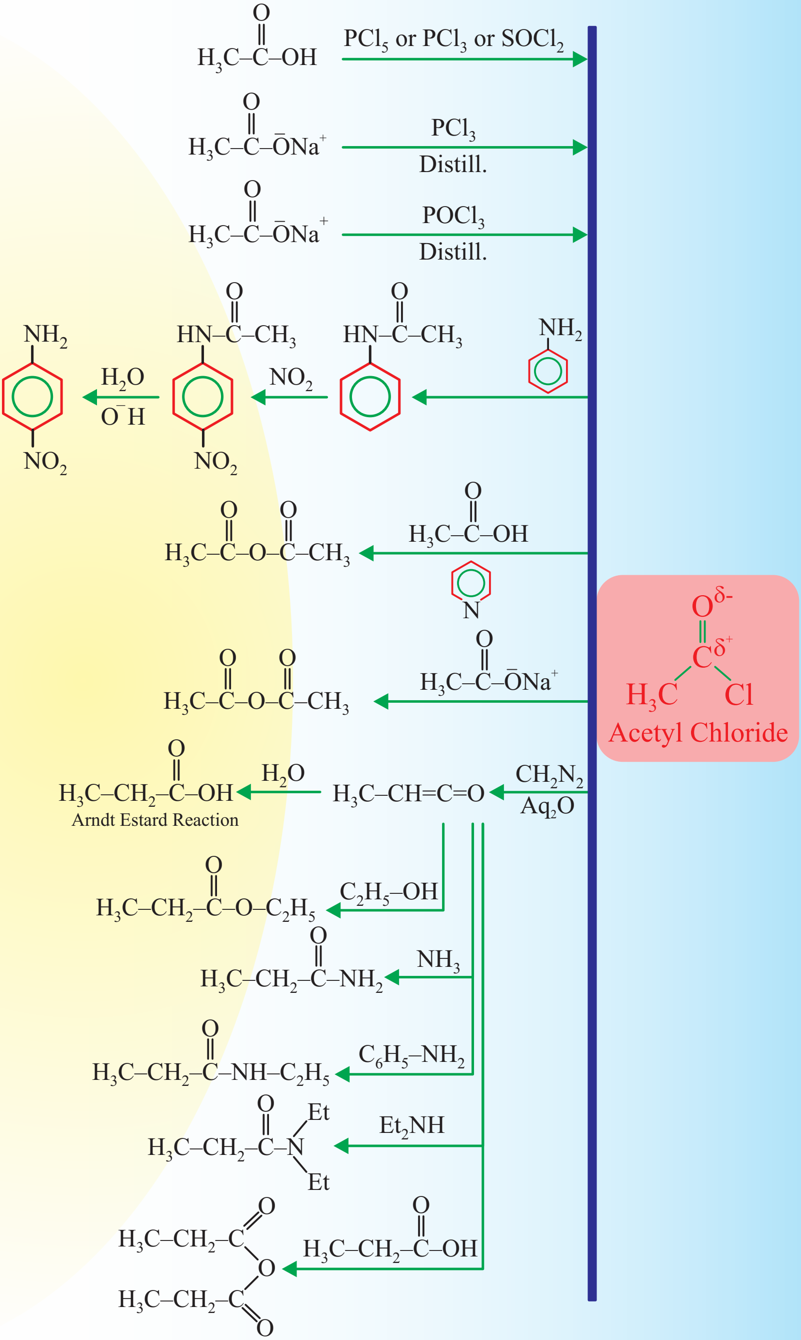
Reactions

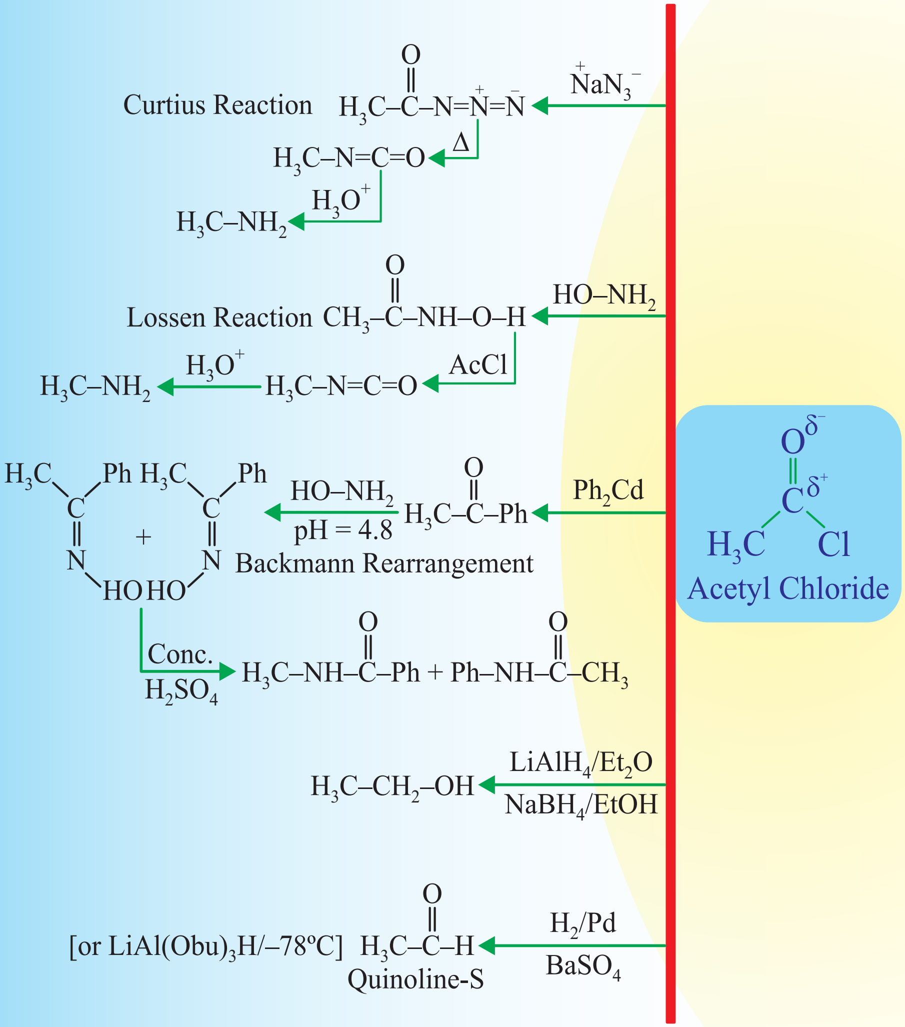


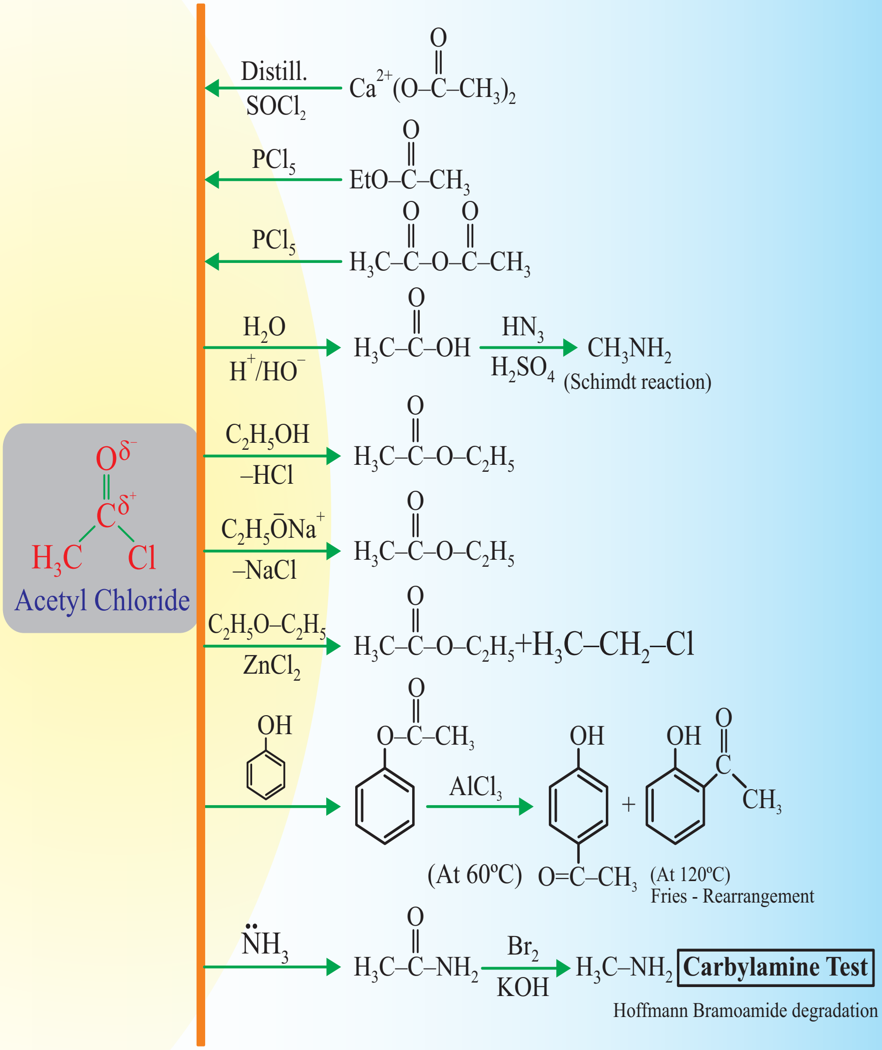
TEST	
Tollen's Reagent	**Fehling solution**
 $H-\overset{\overset{O}{\parallel}}{C}-OH \longrightarrow Ag\downarrow + CO_2\uparrow + H_2O$	 $H-\overset{\overset{O}{\parallel}}{C}-OH \xrightarrow{2CuO} \underset{\text{red ppt.}}{Cu_2O\downarrow} + CO_2 + H_2O$

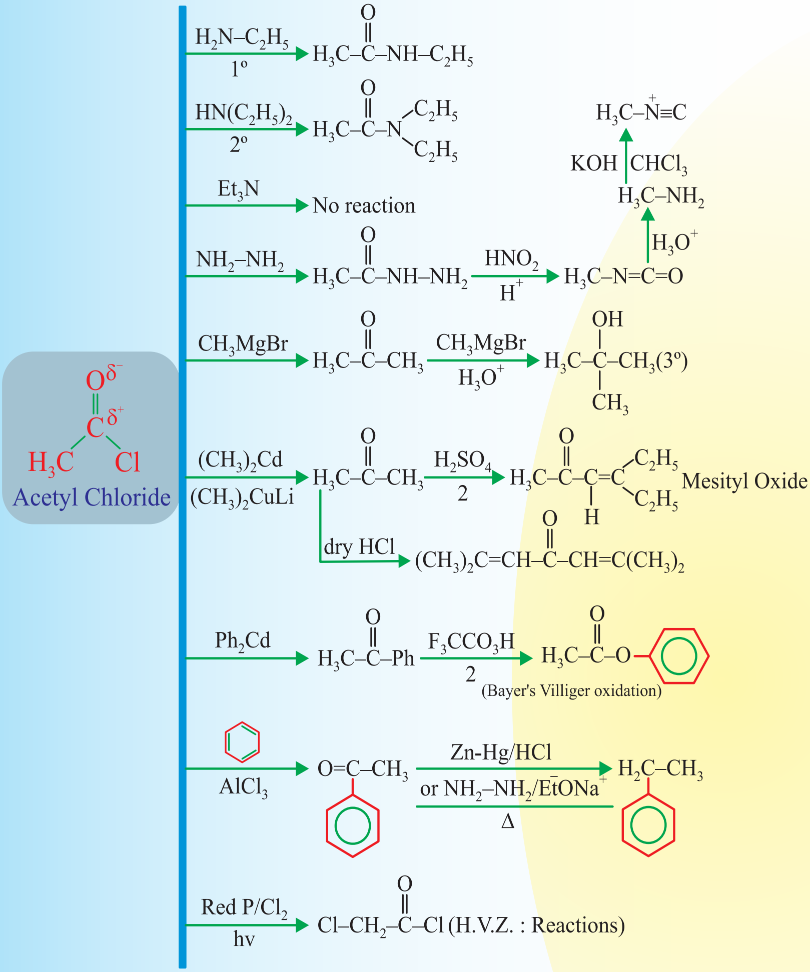


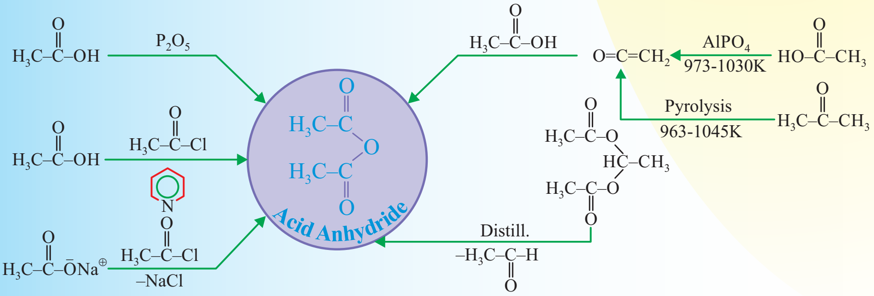


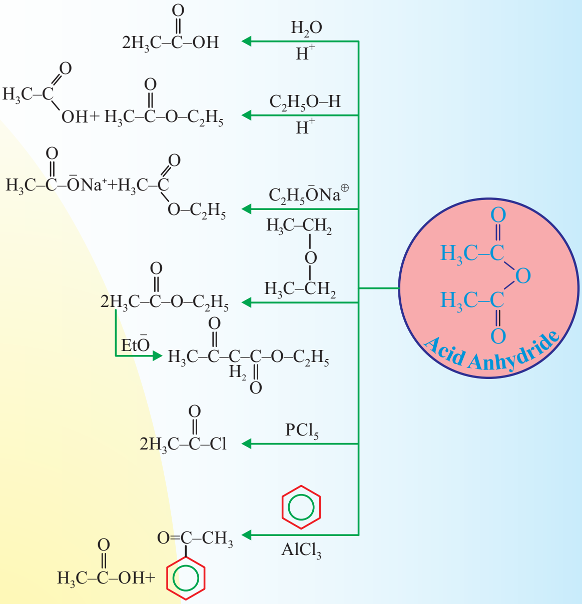

$H_3C-\overset{O}{\overset{\|}{C}}-OH$
PCl_5 or PCl_3 or $SOCl_2$
$H_3C-\overset{O}{\overset{\|}{C}}-\bar{O}Na^+$
PCl_3
Distill.
$H_3C-\overset{O}{\overset{\|}{C}}-\bar{O}Na^+$
$POCl_3$
Distill.
NH_2
$HN-\overset{O}{\overset{\|}{C}}-CH_3$
NO_2
$HN-\overset{O}{\overset{\|}{C}}-CH_3$
NO_2
H_2O
$\bar{O}H$
NH_2
NO_2
$H_3C-\overset{O}{\overset{\|}{C}}-OH$
N
$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$
$O^{\delta-}$
$C^{\delta+}$
H_3C
Cl
Acetyl Chloride
$H_3C-\overset{O}{\overset{\|}{C}}-\bar{O}Na^+$
$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$
CH_2N_2
Aq_2O
$H_3C-CH=C=O$
H_2O
$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-OH$
Arndt Estard Reaction
C_2H_5-OH
$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5$
NH_3
$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-NH_2$
$C_6H_5-NH_2$
$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-NH-C_2H_5$
Et_2NH
$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-N$
Et
Et
$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-OH$
H_3C-CH_2-C
O
O
H_3C-CH_2-C
O

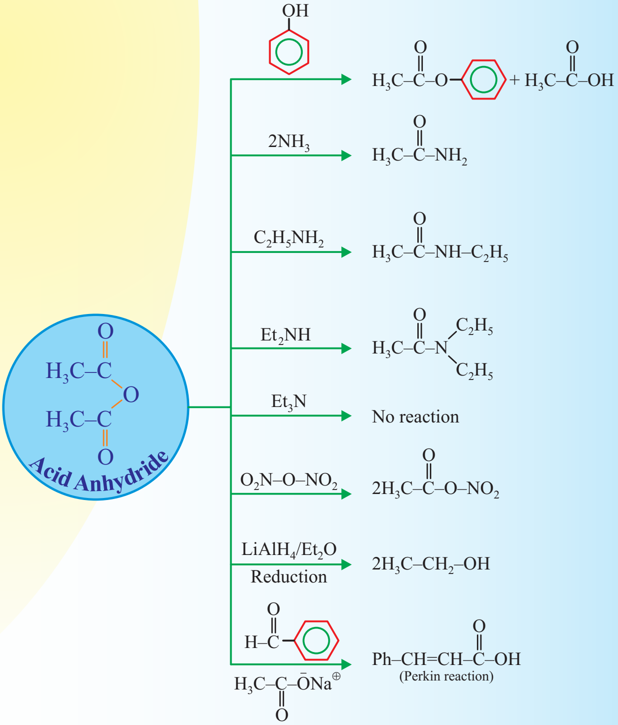

Acetyl Chloride
$H_3C-\overset{O}{\overset{\|}{C}}-Cl$ ($O^{\delta-}$, $C^{\delta+}$)
$\overset{+}{Na}\overset{-}{N_3}$
Curtius Reaction $H_3C-\overset{O}{\overset{\|}{C}}-N=\overset{+}{N}=\overset{-}{N}$
Δ
$H_3C-N=C=O$
H_3O^+
H_3C-NH_2
$HO-NH_2$
Lossen Reaction $CH_3-\overset{O}{\overset{\|}{C}}-NH-O-H$
AcCl
$H_3C-N=C=O$
H_3O^+
H_3C-NH_2
Ph_2Cd
$H_3C-\overset{O}{\overset{\|}{C}}-Ph$
$HO-NH_2$
pH = 4.8
Backmann Rearrangement
H_3C Ph C=N HO + H_3C Ph C=N HO
Conc. H_2SO_4
$H_3C-NH-\overset{O}{\overset{\|}{C}}-Ph + Ph-NH-\overset{O}{\overset{\|}{C}}-CH_3$
$LiAlH_4/Et_2O$
$NaBH_4/EtOH$
H_3C-CH_2-OH
H_2/Pd
$BaSO_4$
Quinoline-S
[or $LiAl(Obu)_3H$/–78°C] $H_3C-\overset{O}{\overset{\|}{C}}-H$


Distill.
SOCl2
Ca2+(O–C–CH3)2
PCl5
EtO–C–CH3
PCl5
H3C–C–O–C–CH3
H2O
H+/HO–
H3C–C–OH
HN3
H2SO4
CH3NH2
(Schimdt reaction)
Oδ–
Cδ+
H3C
Cl
Acetyl Chloride
C2H5OH
–HCl
H3C–C–O–C2H5
C2H5ŌNa+
–NaCl
H3C–C–O–C2H5
C2H5O–C2H5
ZnCl2
H3C–C–O–C2H5+H3C–CH2–Cl
OH
O–C–CH3
AlCl3
OH
OH
C
CH3
+
(At 60ºC)
O=C–CH3
(At 120ºC)
Fries - Rearrangement
N̈H3
H3C–C–NH2
Br2
KOH
H3C–NH2
Carbylamine Test
Hoffmann Bramoamide degradation


Acetyl Chloride
H_3C–C(=$O^{\delta-}$)$^{\delta+}$–Cl
$H_2N–C_2H_5$ 1°
$H_3C–CO–NH–C_2H_5$
$HN(C_2H_5)_2$ 2°
$H_3C–CO–N(C_2H_5)_2$
Et_3N
No reaction
$NH_2–NH_2$
$H_3C–CO–NH–NH_2$
HNO_2 H^+
$H_3C–N=C=O$
H_3O^+
$H_3C–NH_2$
KOH $CHCl_3$
$H_3C–\overset{+}{N}≡C$
CH_3MgBr
$H_3C–CO–CH_3$
CH_3MgBr H_3O^+
$H_3C–C(OH)(CH_3)–CH_3(3°)$
$(CH_3)_2Cd$
$(CH_3)_2CuLi$
$H_3C–CO–CH_3$
H_2SO_4 2
$H_3C–CO–C(H)=C(C_2H_5)_2$
Mesityl Oxide
dry HCl
$(CH_3)_2C=CH–CO–CH=C(CH_3)_2$
Ph_2Cd
$H_3C–CO–Ph$
F_3CCO_3H 2
$H_3C–CO–O–$
(Bayer's Villiger oxidation)
$AlCl_3$
$O=C–CH_3$
Zn-Hg/HCl
or $NH_2–NH_2/\bar{E}tONa^+$
Δ
$H_2C–CH_3$
Red P/Cl_2
hv
$Cl–CH_2–CO–Cl$ (H.V.Z. : Reactions)

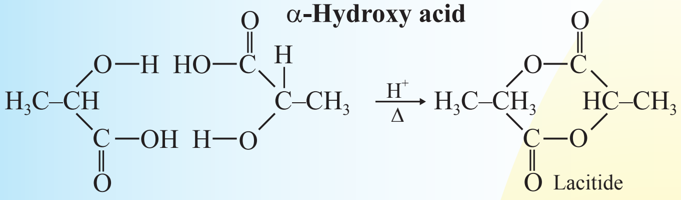

$H_3C–CO–OH$
P_2O_5
$H_3C–CO–OH$
$H_3C–CO–Cl$
N
$H_3C–CO–\bar{O}Na^{\oplus}$
$H_3C–CO–Cl$
–NaCl
$H_3C–CO–O–CO–CH_3$
Acid Anhydride
$H_3C–CO–OH$
$O=C=CH_2$
$AlPO_4$
973-1030K
$HO–CO–CH_3$
Pyrolysis
963-1045K
$H_3C–CO–CH_3$
$H_3C–CO–O–HC(CH_3)–O–CO–CH_3$
Distill.
$–H_3C–CO–H$


Acid Anhydride
H2O, H+ → 2H3C–C(=O)–OH
C2H5O–H, H+ → H3C–C(=O)OH + H3C–C(=O)–O–C2H5
C2H5ŌNa⊕ → H3C–C(=O)–ŌNa+ + H3C–C(=O)–O–C2H5
H3C–CH2–O–CH2–CH3 → 2H3C–C(=O)–O–C2H5
EtŌ → H3C–C(=O)–CH2–C(=O)–O–C2H5
PCl5 → 2H3C–C(=O)–Cl
AlCl3 → O=C–CH3 + H3C–C(=O)–OH

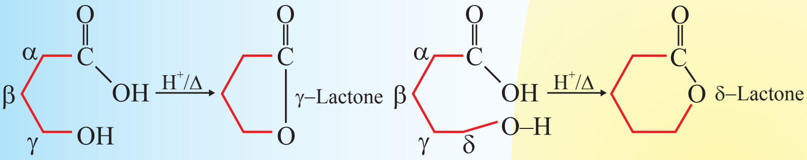

Acid Anhydride
OH → H3C–C(=O)–O– + H3C–C(=O)–OH
2NH3 → H3C–C(=O)–NH2
C2H5NH2 → H3C–C(=O)–NH–C2H5
Et2NH → H3C–C(=O)–N(C2H5)(C2H5)
Et3N → No reaction
O2N–O–NO2 → 2H3C–C(=O)–O–NO2
LiAlH4/Et2O
Reduction → 2H3C–CH2–OH
H–C(=O)– , H3C–C(=O)–ŌNa⊕ → Ph–CH=CH–C(=O)–OH
(Perkin reaction)

Heating Effect

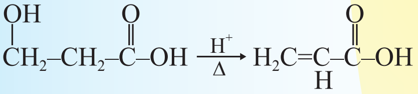
α-Hydroxy acid



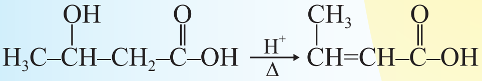
γ & α-Hydroxy acid



β-Hydroxy acid

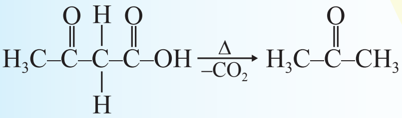


$\overset{OH}{\overset{|}{CH_2}}-CH_2-\overset{O}{\overset{||}{C}}-OH \xrightarrow[\Delta]{H^+} H_2C=\underset{H}{C}-\overset{O}{\overset{||}{C}}-OH$

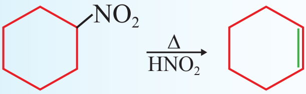


$H_3C-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-OH \xrightarrow[\Delta]{H^+} \overset{CH_3}{\overset{|}{CH}}=CH-\overset{O}{\overset{||}{C}}-OH$

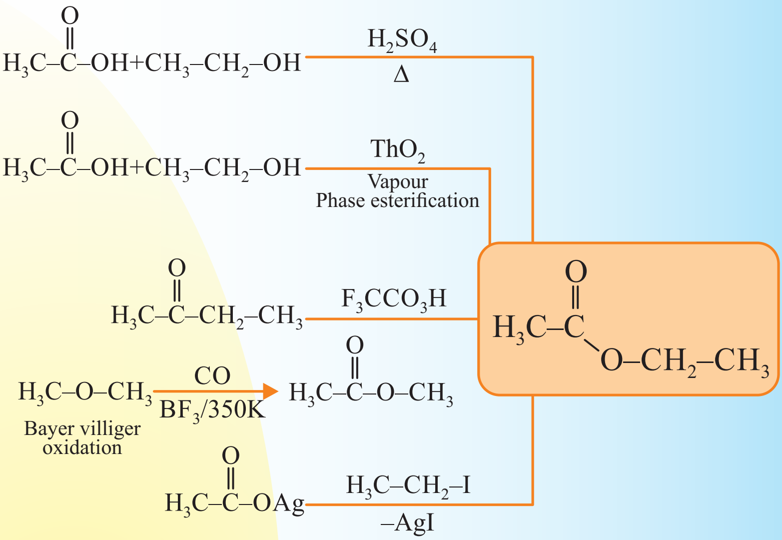
β-Keto acid



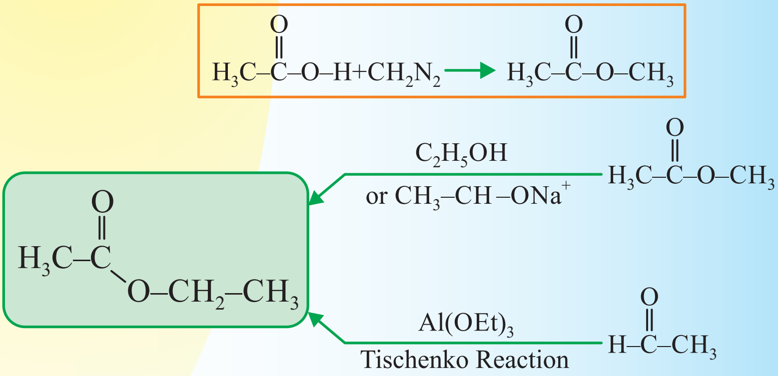
$H_3C-\overset{O}{\overset{||}{C}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{O}{\overset{||}{C}}-OH \xrightarrow[-CO_2]{\Delta} H_3C-\overset{O}{\overset{||}{C}}-CH_3$



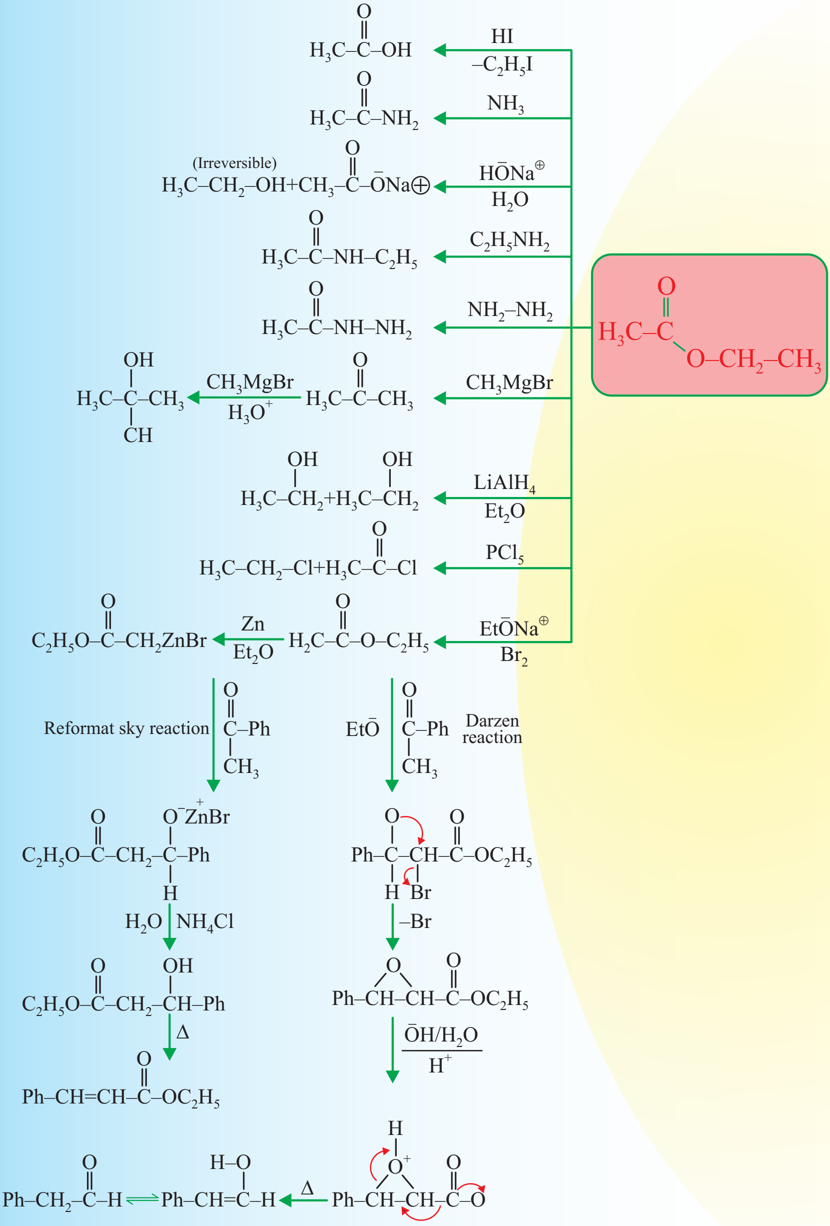
Nutshell preparation of Ester



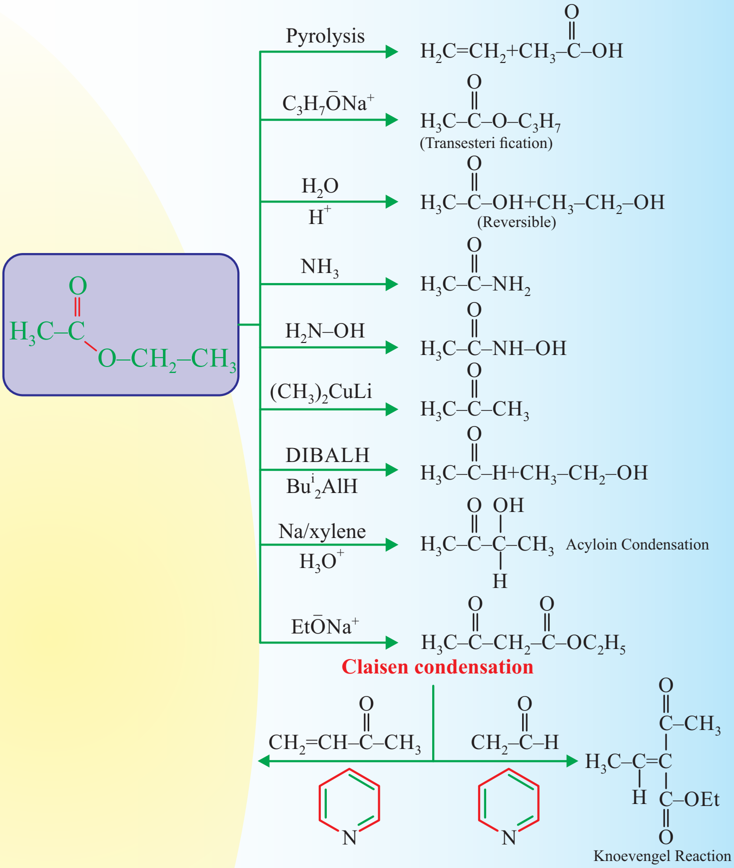
Nutshell preparation of Ester



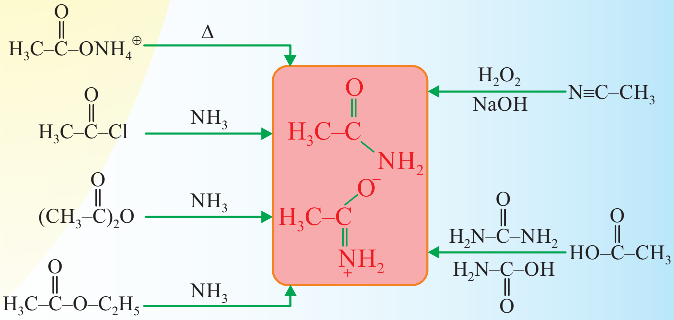
Nutshell Chemical Properties of Ester



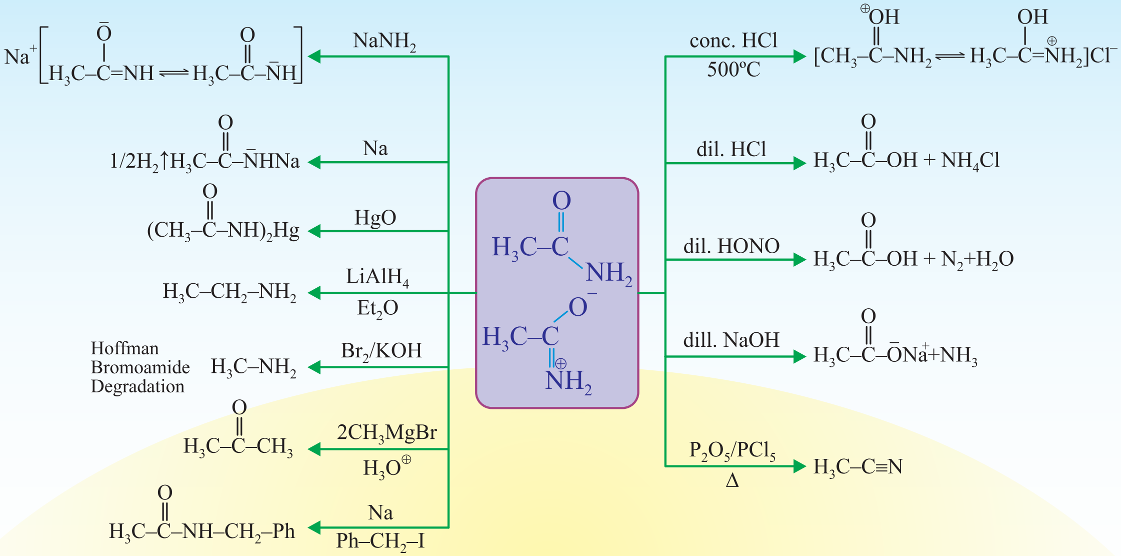
Nutshell Chemical Properties of Ester



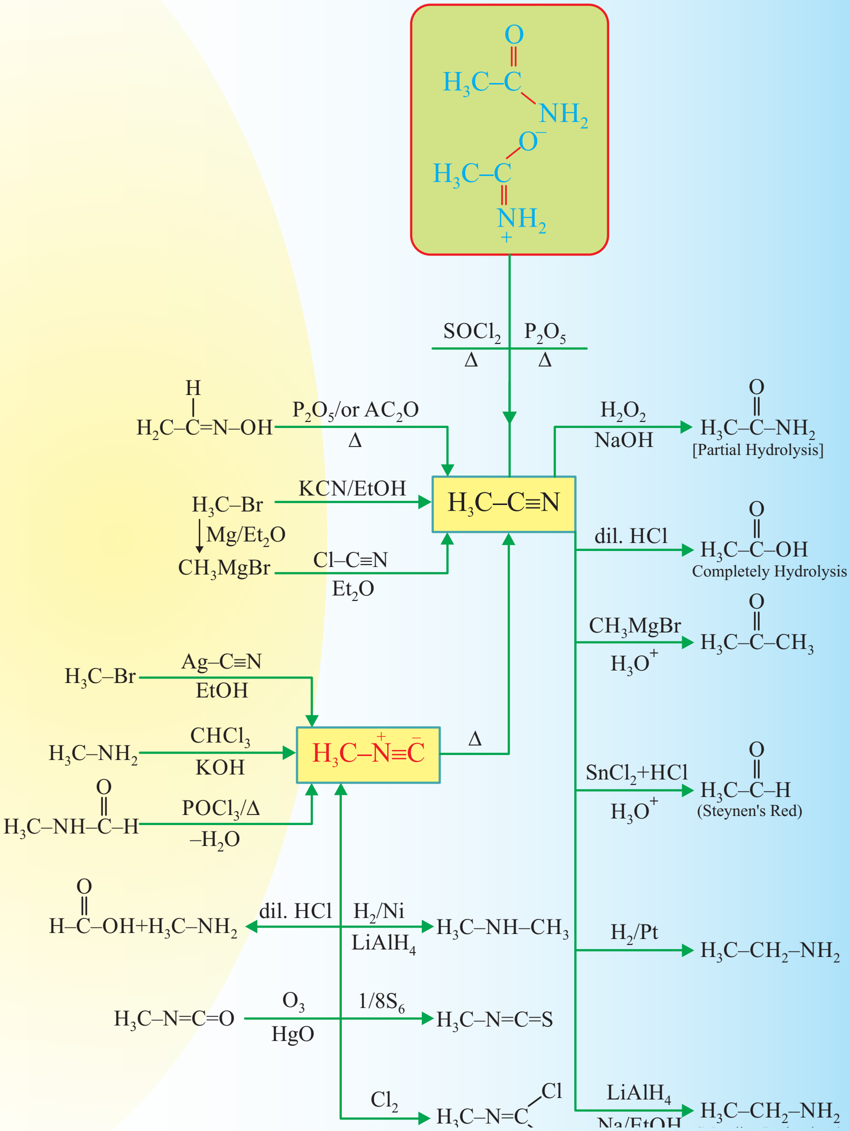
Nutshell preview and review of Amide, Cyanide and Isocyanide



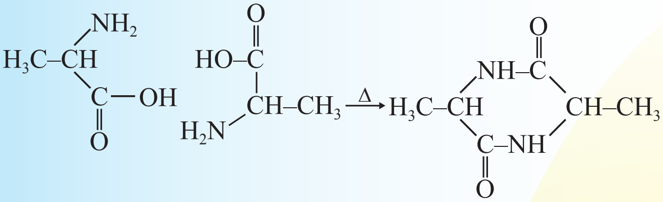
Nutshell preview and review of Amide, Cyanide and Isocyanide

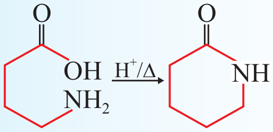


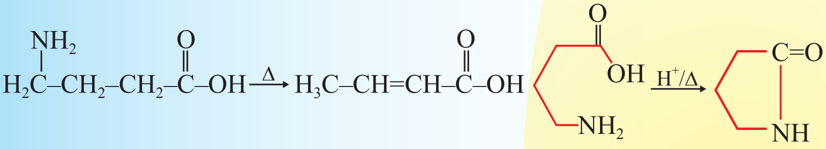
Nutshell preview and review of Amide, Cyanide and Isocyanide



Amino Acid:







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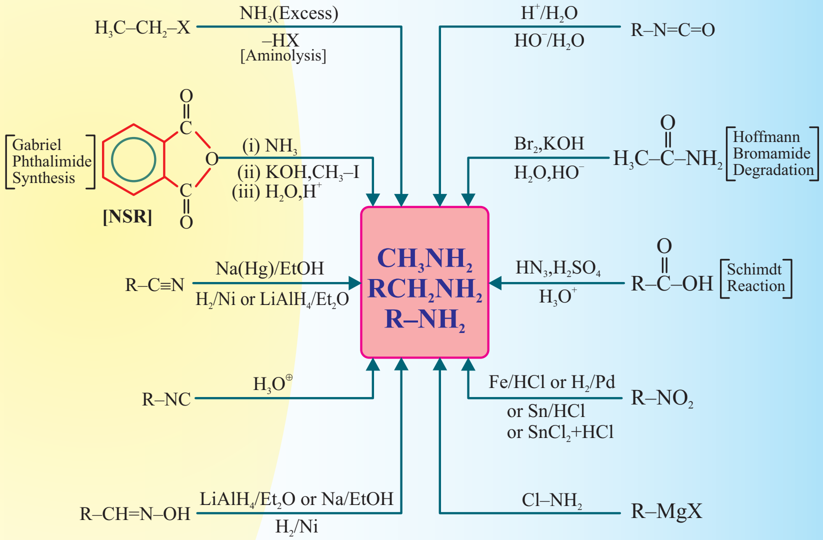
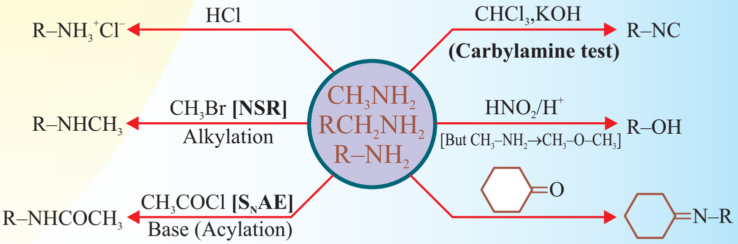
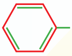
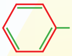
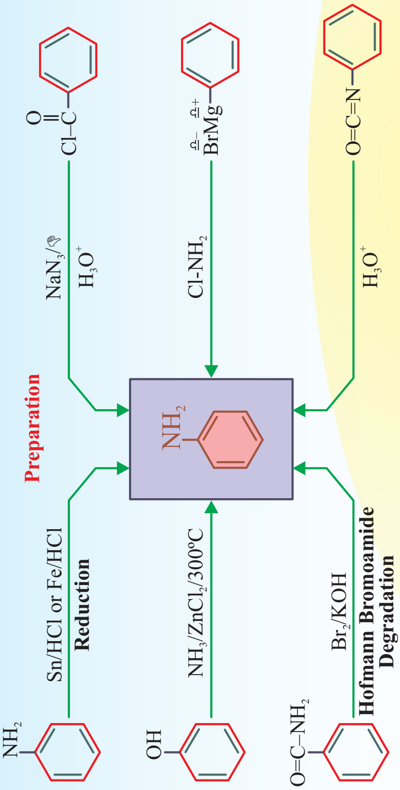
CHAPTER 19

Amines

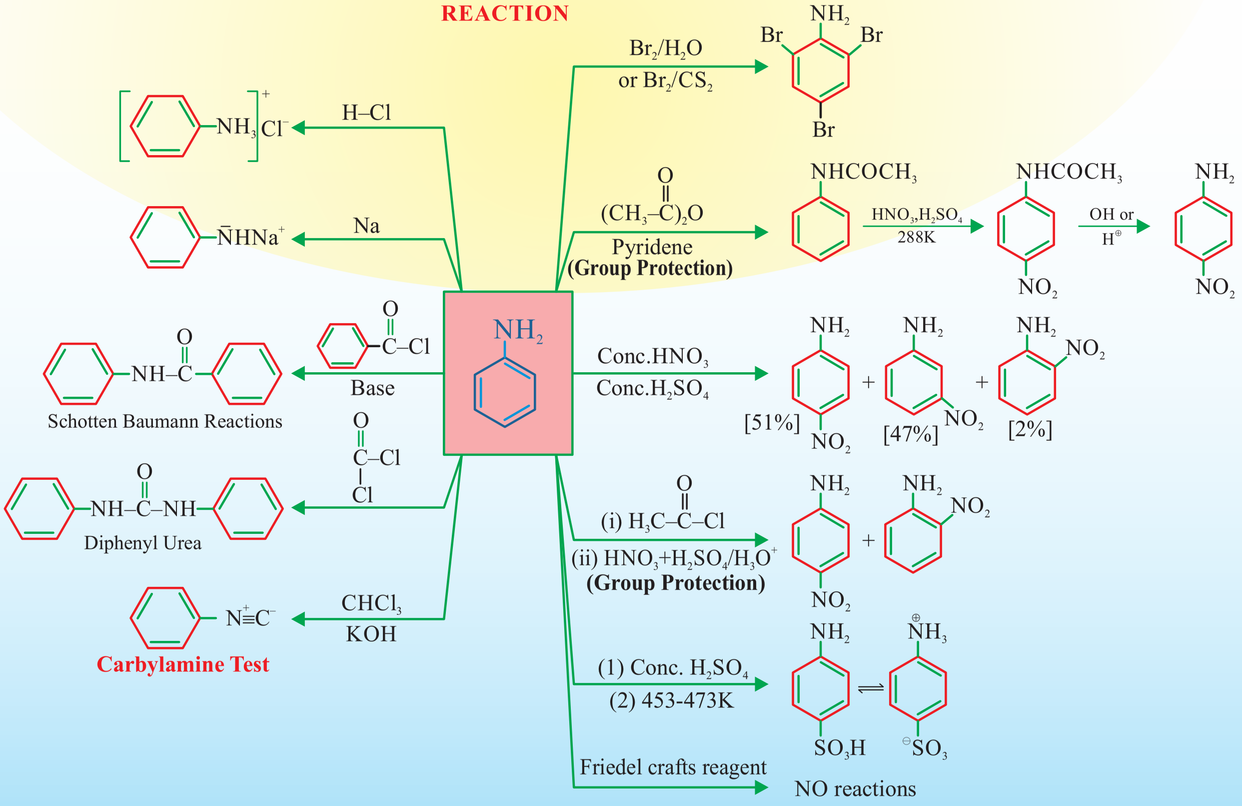




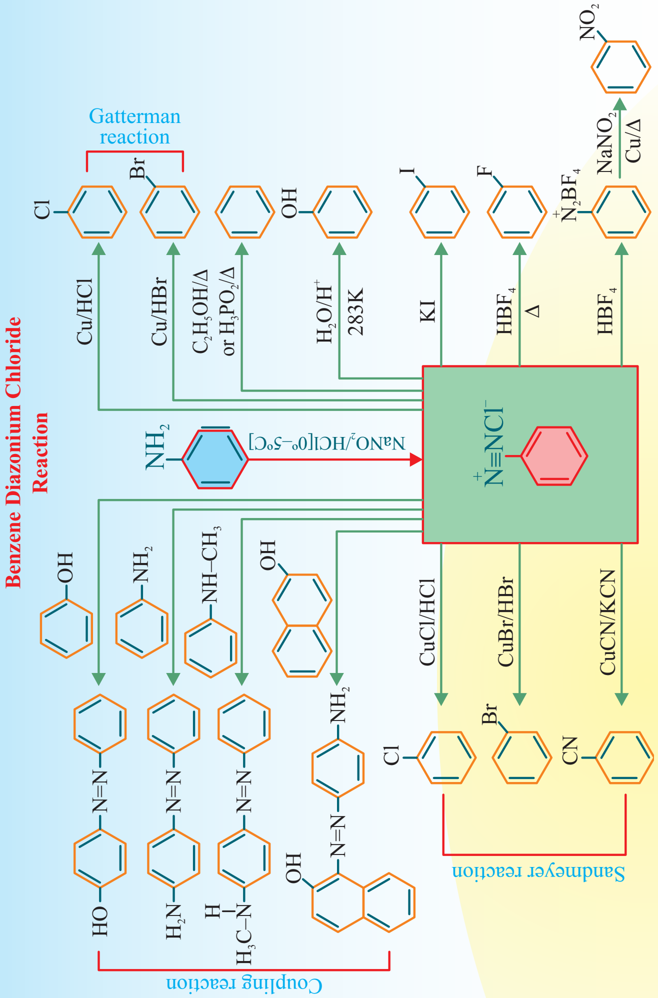
Test				
Reagent	R–N̈H$_2$(1°)	R$_2$N̈H(2°)	R$_3$N̈(3°)	 N̈H$_2$
Ph–SO$_2$Cl (Hinsberg reagent)	$\underset{\text{H}}{\text{R–N}}\text{–SO}_2\text{–Ph}$ soluble $\downarrow$ NaOH $[\text{R–}\overset{\ominus}{\text{N}}\text{–SO}_2\text{–Ph}]\text{Na}^+$	$\text{R}_2\text{N–}\underset{\text{O}}{\overset{\text{O}}{\text{S}}}\text{–Ph}$ $\downarrow$ NaOH Insoluble	No reaction	 NH–SO$_2$–Ph
$\overset{\text{S}}{\overset{\|}{\text{C}}}\text{=S}$ Δ/HgCl$_2$ Mustard oil test	$\text{R–NH–}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{–SH}$ HgCl$_2$ $\downarrow$ Δ R–N=C=S+HgS	$\text{R}_2\text{N–}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{–SH}$ HgCl$_2$ $\downarrow$ Δ No reaction	No reaction	$\xrightarrow{\text{KOH}}$ Ph–N=C=S+HgS



REACTION



NH2
Br2/H2O
or Br2/CS2
Br
Br
Br
O
(CH3–C)2O
Pyridene
(Group Protection)
NHCOCH3
HNO3,H2SO4
288K
NHCOCH3
NO2
OH or
H⊕
NH2
NO2
Conc.HNO3
Conc.H2SO4
[51%]
[47%]
[2%]
(i) H3C–C–Cl
(ii) HNO3+H2SO4/H3O+
(Group Protection)
(1) Conc. H2SO4
(2) 453-473K
SO3H
⊕NH3
⊖SO3
Friedel crafts reagent
NO reactions
H–Cl
NH3 Cl–
Na
N̄HNa+
Base
C–Cl
NH–C
Schotten Baumann Reactions
C–Cl
Cl
NH–C–NH
Diphenyl Urea
CHCl3
KOH
N≡C–
Carbylamine Test

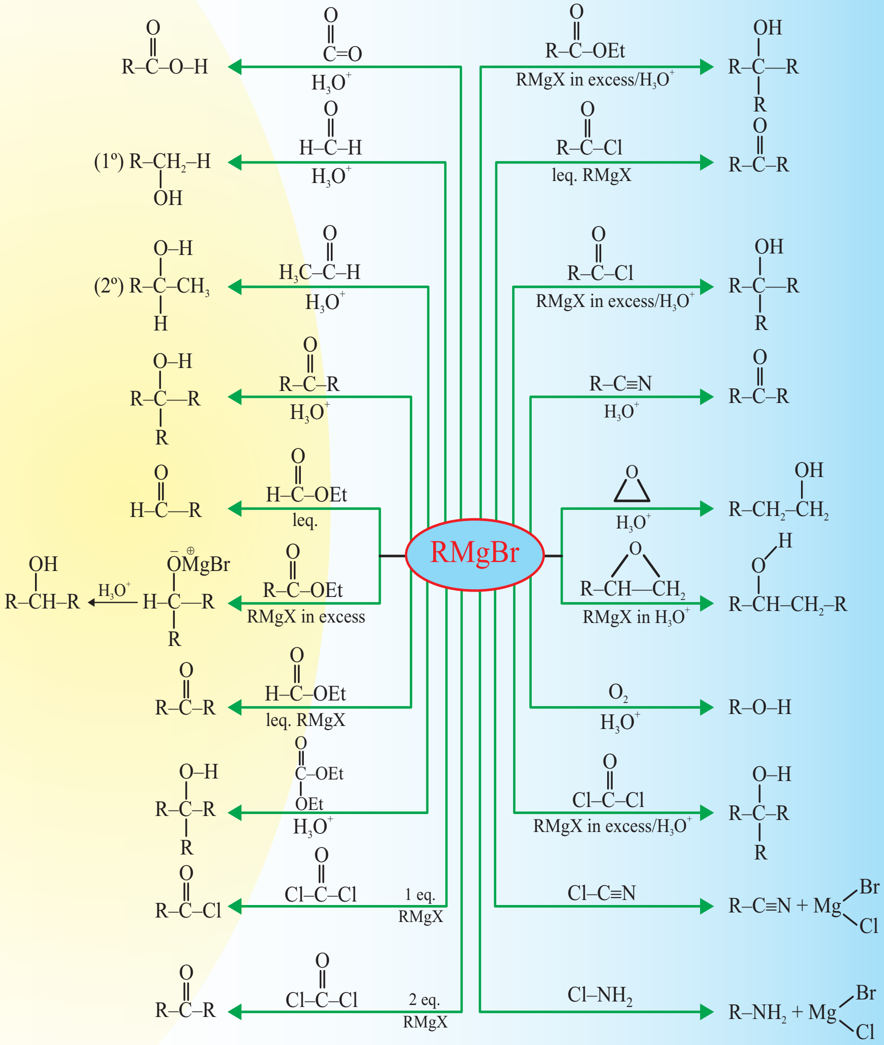


FrSR	Free Radical Substitution reaction
ESR	Electrophilic Substitution reaction
NSR	Nucleophilic Substitution reaction
S_NAE	Substitution Nucleophilic (addition elimination)
FrAR	Free radical addition reaction
NAR	Nucleophilic addition reaction
EAR	Electrophilic addition reaction
FrER	Free Radical Elimination reaction

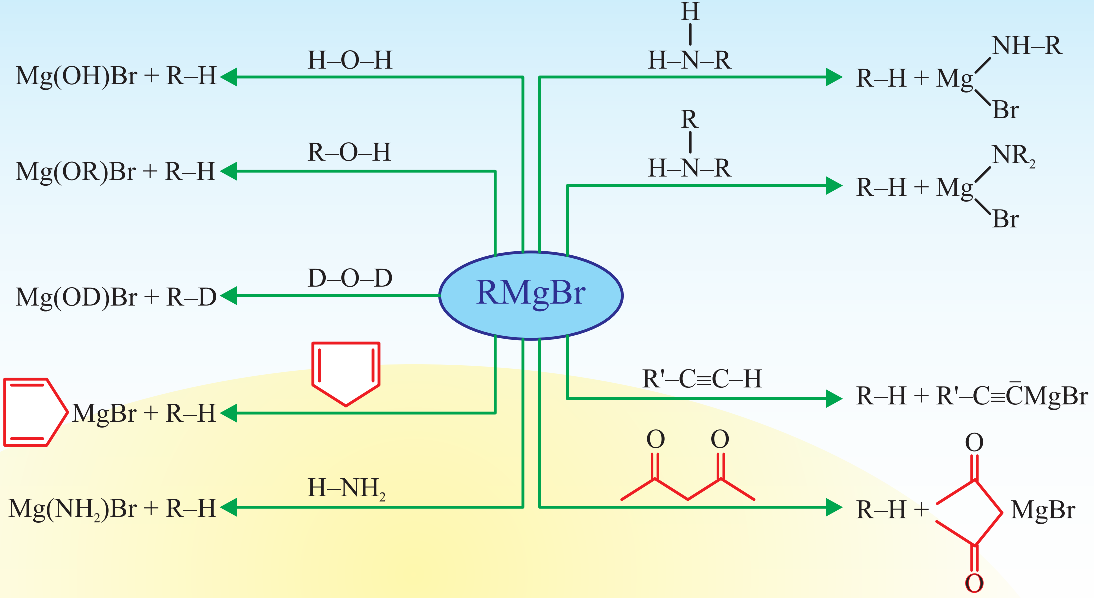
GRIGNARD REAGENT

REACTION

GRIGNARD REAGENT as Nucleophile



GRIGNARD REAGENT as Base (Active H-containing compound)



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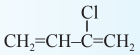
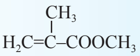
CHAPTER

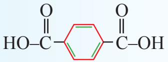
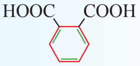
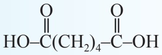
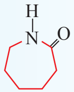
20

Polymers

ADDITION POLYMERS			
S.No	**Name of Polymer**	**Starting Materials**	**Nature of Polymer**
I. Polyolefins			
1.	Polyethylene or Polyethene	$CH_2=CH_2$	Low density homopolymer (branched chain growth)
2.	Polypropylene or Polypropene	$CH_3CH=CH_2$	Homopolymer, linear, chain growth
3.	Polystyrene	$C_6H_5CH=CH_2$	Homopolymer, linear, chain growth
II. Polydiences			
1.	Neoprene	 $CH_2=CH-\overset{\overset{\displaystyle Cl}{\vert}}{C}=CH_2$ Chloroprene or 1-Chloro-1,3-butadiene	Homopolymer, chain growth
2.	Buna S (Styrene-Butadiene, Rubber SBR or GRS)	$CH_2=CH-CH=CH_2$ and 1,3-butadiene $C_6H_5CH=CH_2$ Styrene	Copolymer, chain growth
III. Polyacrylates			
1.	Polymethylmethacrylate (Flexiglss Lucite, Acrylite or Perspex PMMA)	 $H_2C=\overset{\overset{\displaystyle CH_3}{\vert}}{C}-COOCH_3$	Homopolymer
2.	Polyethylacrylate	$H_2C=CH-COOC_2H_5$	Homopolymer
3.	Polyacrylonitrile or Orlon PAN	$CH_2=CH-CN$	Homopolymer

IV. Polyhalofins			
1.	Polyvinyl chloride PVC	$CH_2=CH-Cl$	Homopolymer, chain growth
2.	Polytetrafluoroethylene or Teflon PTFE	$F_2C=CF_2$	Homopolymer
3.	Polymonochlorotrifluoroethylene PCTFE	$ClFC=CF_2$	Homopolymer

CONDENSATION POLYMERS

S.No	Name of Polymer	Starting Materials	Nature of Polymer
I. Polyesters			
1.	Terylene or Dacron	$HO-CH_2-CH_2-OH$ 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	$HO-CH_2-CH_2-OH$ Ethylene glycol and  Phthalic acid or Benzene-1,2-dicarboxylic acid	Copolymer, linear step growth
II. Polyamides			
1.	Nylon-6,6	 $HO-\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH$ Adipic acid and $H_2N-(CH_2)_6-NH_2$ Hexamethylenediamine	Copolymer, linear, step growth
2.	Nylon-6,10	$H_2N(CH_2)_6NH_2$ Hexamethylene diamine and $HOOC(CH_2)_8COOH$ Sebacic acid	Copolymer, linear, step growth
3.	Nylon-6	 Caprolactum	Homopolymer, linear
Formaldehyde resins			
1.	Phenolformaldehye resin or Bakelite	Phenol and formaldehyde	Copolymer, step growth
2.	Melamine formaldehyde resin	Melamine and formaldehyde	Copolymer, step growth

CHAPTER 21

Biomolecules

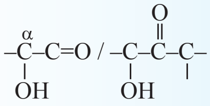
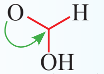
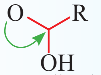
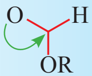
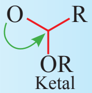
- Carbohydrates are defined as optically active polyhydroxy aldehydes or ketones or the compound which produce such units on hydrolysis.
- **Monosaccharide ($C_nH_{2n}O_n$):** Single unit, can't be hydrolysed : Glucose and fructose.
- **Oligosaccharides** gives two to ten monosaccharides on hydrolysis.
- **Disaccharides** (by glycosidic linkage)

  Sucrose $\xrightarrow{H_3O^+}$ α–D. Glucose + β–D. Fructose;

  Maltose $\xrightarrow{H_3O^+}$ 2 α–D. Glucose unit

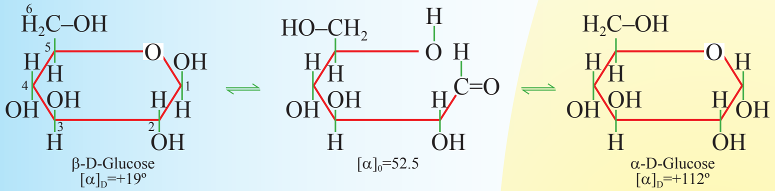
  Lactose $\xrightarrow{H_3O^+}$ β–D. Glucose + β–D. Galactose.
- **Polysaccharide:** Contain more than ten monosaccharide units.

  $(C_6H_{10}O_5)_n$: 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	 $\overset{\alpha}{\underset{\vert\;\text{OH}}{-\text{C}}}-\text{C}=\text{O}$ / $-\underset{\vert\;\text{OH}}{\text{C}}-\overset{\overset{\text{O}}{\Vert}}{\text{C}}-\underset{\vert}{\text{C}}-$  Hemiacetal  Hemiketal	 Acetal  Ketal

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

- **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 (± 52.5°) is reached.



β-D-Glucose $[\alpha]_D = +19°$

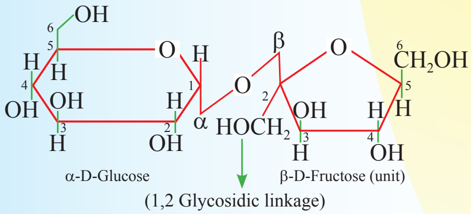
$[\alpha]_0 = 52.5$

α-D-Glucose $[\alpha]_D = +112°$

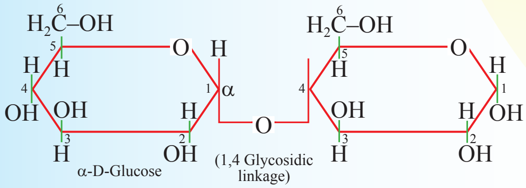
- **Anomer's:** Differ in configuration at 1st carbon due to hemi (acetal or ketal)ring formation. The new-asymmetric carbon is referred to as Anomeric carbon.
- **Epimer's:** Diastereomer's which differ in conformation at any one chiral carbon.

  eg. D-Glucose & D-mannose

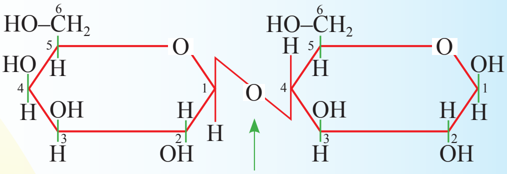
  D-Glucose & D-Galactose
- **Sucrose:**



- **Maltose:**



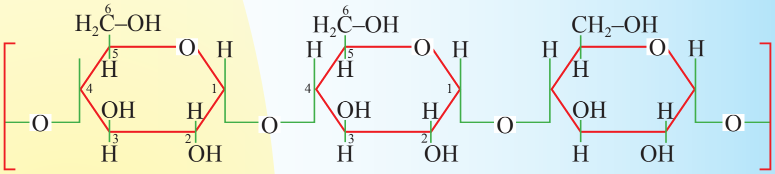
- **Lactose**



(1,4 Glycosidic linkage)

Starch: (Amylose & Amylopectin)

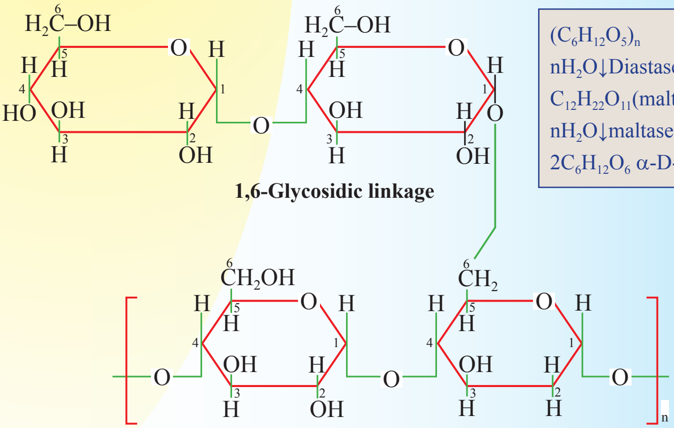
- **Amylose (*Straight Chain*)**



(α-1,4 Glycosidic linkage)

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

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



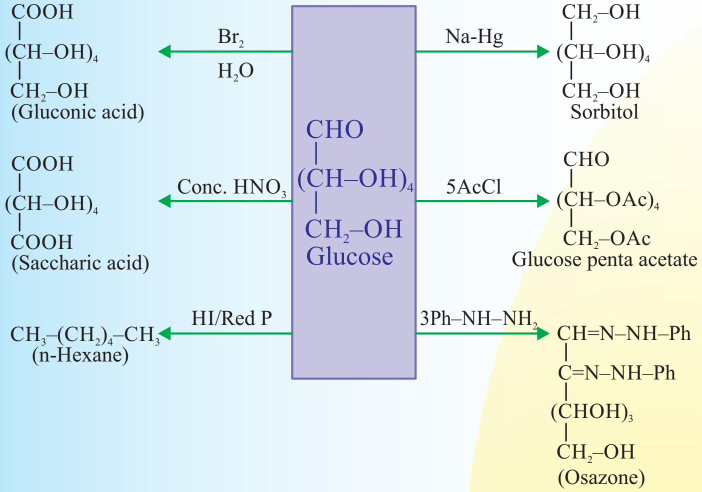
1,6-Glycosidic linkage

1,4 Glycosidic linkage

$(C_6H_{12}O_5)_n$
$nH_2O\downarrow$Diastase
$C_{12}H_{22}O_{11}$(maltose)
$nH_2O\downarrow$maltase
$2C_6H_{12}O_6$ α-D-Glucose

Cellulose
$nH_2O\downarrow$
$nC_6H_{12}O_6$
β-D-Glucose

REACTION OF GLUCOSE (OPEN CHAIN STRUCTURE)



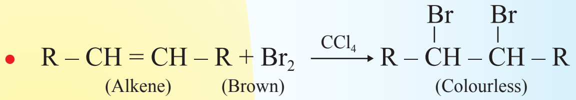
CHAPTER

22

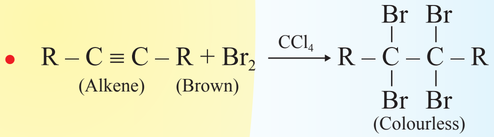
Distinction between Pairs of Compounds

UNSATURATION TEST

(a) Double/Triple bonded Compounds (C=C)/(C≡C) + Br_2 in CCl_4 (Brown colour) → Colourless compound.

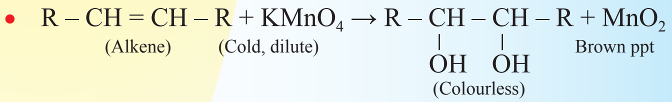


$$\bullet\ \underset{\text{(Alkene)}}{R-CH=CH-R} + \underset{\text{(Brown)}}{Br_2} \xrightarrow{CCl_4} \underset{\text{(Colourless)}}{R-\overset{\overset{\displaystyle Br}{|}}{CH}-\overset{\overset{\displaystyle Br}{|}}{CH}-R}$$



$$\bullet\ \underset{\text{(Alkene)}}{R-C\equiv C-R} + \underset{\text{(Brown)}}{Br_2} \xrightarrow{CCl_4} \underset{\text{(Colourless)}}{R-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle Br}{|}}{C}}-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle Br}{|}}{C}}-R}$$

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



$$\bullet\ \underset{\text{(Alkene)}}{R-CH=CH-R} + \underset{\text{(Cold, dilute)}}{KMnO_4} \rightarrow \underset{\text{(Colourless)}}{R-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH}-R} + \underset{\text{Brown ppt}}{MnO_2}$$

- $R-C\equiv C-R' + \underset{\text{(Hot, dilute)}}{KMnO_4} \rightarrow \underset{\text{Brown ppt.}}{MnO_2} + RCOOH\ \ R'COOH$

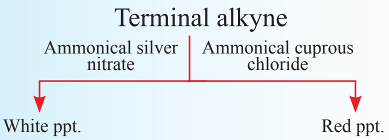
- $\underset{\text{(Alkyne)}}{R-C\equiv C-H} + \underset{\text{(Hot, dilute)}}{KMnO_4} \rightarrow \underset{\text{Brown ppt.}}{MnO_2} + RCOOH + \underset{\text{(Colourless)}}{CO_2 + H_2O}$

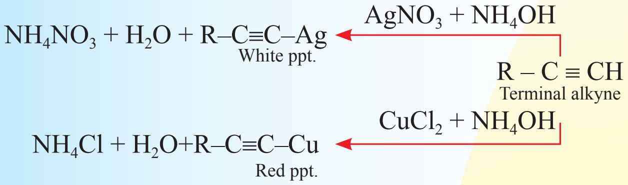
Baeyer's reagent is cold, dilute $KMnO_4$ solution having pink colour.

NOTES

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

TEST FOR TERMINAL ALKYNE





$$NH_4NO_3 + H_2O + \underset{\text{White ppt.}}{R{-}C{\equiv}C{-}Ag} \xleftarrow{AgNO_3 + NH_4OH} \underset{\text{Terminal alkyne}}{R - C \equiv CH}$$

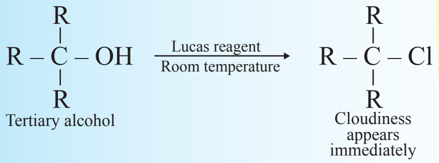
$$NH_4Cl + H_2O + \underset{\text{Red ppt.}}{R{-}C{\equiv}C{-}Cu} \xleftarrow{CuCl_2 + NH_4OH} \underset{\text{Terminal alkyne}}{R - C \equiv CH}$$

NATURE OF X-GROUP IN C-X BOND

$$R{-}X + \text{aqueous } KOH \rightarrow R{-}OH + KX \xrightarrow[AgNO_3]{HNO_3} \underset{\text{(Precipitate)}}{AgX}$$

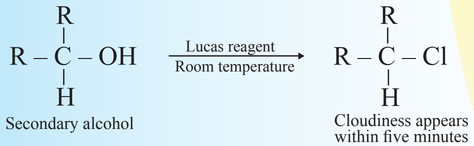
If X is Cl, precipitate will be white and for Br yellow precipitate will be obtained.

DISTINCTION BETWEEN 1°, 2° AND 3° ALCOHOL

- 

  $$\underset{\text{Tertiary alcohol}}{R - \overset{\displaystyle R}{\underset{\displaystyle R}{C}} - OH} \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} R - \overset{\displaystyle R}{\underset{\displaystyle R}{C}} - Cl$$

  Cloudiness appears immediately

- 

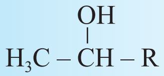
  $$\underset{\text{Secondary alcohol}}{R - \overset{\displaystyle R}{\underset{\displaystyle H}{C}} - OH} \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} R - \overset{\displaystyle R}{\underset{\displaystyle H}{C}} - Cl$$

  Cloudiness appears within five minutes

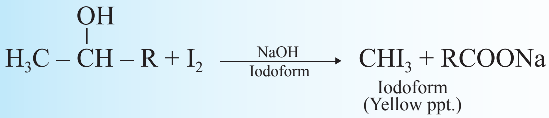
- $\underset{\text{Primary alcohol}}{R - CH_2 - OH} \xrightarrow[\text{Heat}]{\text{Lucas reagent}} R - CH_2 - Cl$

  Cloudiness appears after 30 minute

Lucas reagent is anhydrous $ZnCl_2$ + conc. HCl.

- 

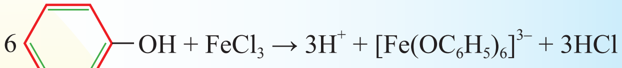
  $H_3C - \overset{\displaystyle OH}{CH} - R$ type of alcohols give iodoform test.

- 

  $$H_3C - \overset{\displaystyle OH}{CH} - R + I_2 \xrightarrow[\text{Iodoform}]{NaOH} \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3} + RCOONa$$

PHENOL

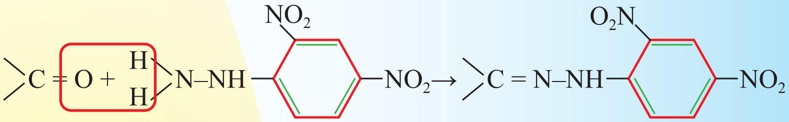
$$\text{Phenol} + \underset{\text{(neutral)}}{\text{ferric chloride}} \rightarrow \text{Violet colouration}$$



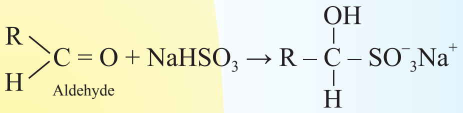
Violet colouration

CARBONYL GROUP

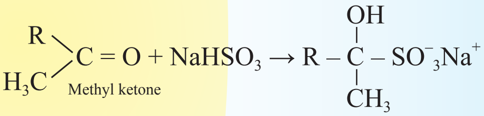
- Carbonyl compound + 2, 4-Dinitrophenylhydrazine → Yellow/orange crystal (Brady's reagent)



- All aldehydes and only aliphatic methyl ketones + $NaHSO_3$ → White crystalline bisulphite.



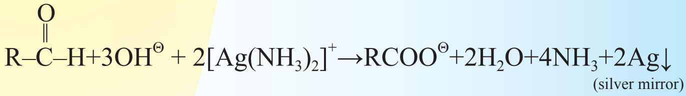
$$\underset{\text{Aldehyde}}{R(H)C=O} + NaHSO_3 \rightarrow R-\overset{OH}{\underset{H}{C}}-SO_3^-Na^+$$



$$\underset{\text{Methyl ketone}}{R(H_3C)C=O} + NaHSO_3 \rightarrow R-\overset{OH}{\underset{CH_3}{C}}-SO_3^-Na^+$$

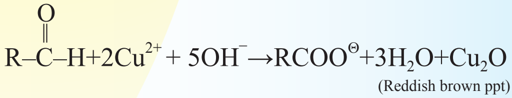
ALDEHYDE GROUP

- Aldehyde + Tollen's reagent → Silver mirror



$$R-\overset{O}{\overset{\|}{C}}-H + 3OH^{\ominus} + 2[Ag(NH_3)_2]^+ \rightarrow RCOO^{\ominus} + 2H_2O + 4NH_3 + \underset{\text{(silver mirror)}}{2Ag\downarrow}$$

- Aldehyde + Fehling's solution → Reddish brown precipitate



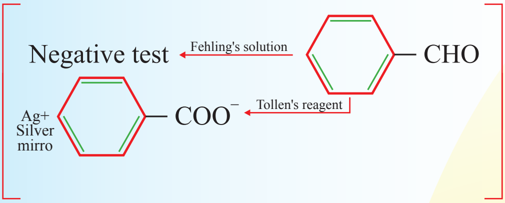
$$R-\overset{O}{\overset{\|}{C}}-H + 2Cu^{2+} + 5OH^- \rightarrow RCOO^{\ominus} + 3H_2O + \underset{\text{(Reddish brown ppt)}}{Cu_2O}$$

- $H_3C-\overset{O}{\overset{\|}{C}}-$ group also give iodoform test

$$H_3C-\overset{O}{\overset{\|}{C}}-R + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3} + RCOONa$$

AROMATIC ALDEHYDE GROUP

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



CARBOXYLIC GROUP

Carboxylic acid + Sodium bicarbonate → effervescence

$RCOOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2\uparrow$

FORMIC ACID

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{\text{Fehling's solution}} H_2O + CO_3^{2-} + \underset{\text{Red ppt.}}{Cu_2O}$$

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{\text{Tollen's reagent}} \underset{\text{Silver mirror}}{2Ag} + CO_3^{2-} + H_2O$$

AMINES (1°)

$$\text{Primary amine} + KOH + CHCl_3 \xrightarrow[\text{reaction}]{\text{Carbylamine}} \underset{\text{(Offensive smell)}}{\text{Isonitrile}}$$

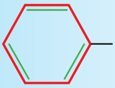
Amines (1°, 2°& 3°) (Hinsberg's test)

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

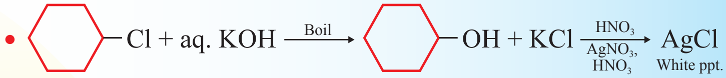
NOTES

Benzenesulphonyl chloride is called Hinsberg's reagent.

Chloroethane and Chlorobenzene

- $C_2H_5\text{–}Cl + \text{aq } KOH \xrightarrow{\text{Boil}} C_2H_5\text{–}OH + KCl \xrightarrow[AgNO_3]{HNO_3} \underset{\text{White ppt.}}{AgCl}$
- 
  $\text{–}Cl + \text{aq. } KOH \xrightarrow[\text{AgNO}_3,\ \text{HNO}_3]{\text{Boil}} \text{No reaction}$

Chlorocyclohexane and chlorobenzene

- 

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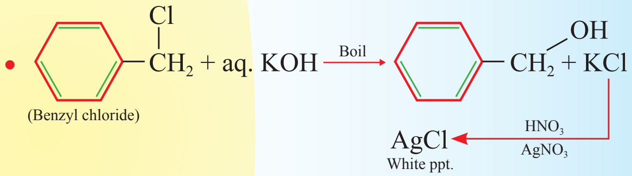
Chlorocyclohexane and bromoethane

- $C_2H_5\text{–}Cl + aq.\ KOH \xrightarrow{\text{Boil}} C_2H_5\text{–}OH + KCl \xrightarrow[\text{AgNO}_3]{\text{HNO}_3} AgCl$
  (Chloroethane) White ppt.

- $C_2H_5\text{–}Br + aq.\ KOH \xrightarrow{\text{Boil}} C_2H_5\text{–}OH + KBr \xrightarrow[\text{AgNO}_3]{\text{HNO}_3} AgBr$
  (Bromoethane) Yellow ppt.

Benzyl chloride and chlorobenzene

- 

(Benzyl chloride)

- 

Chlorobenzene

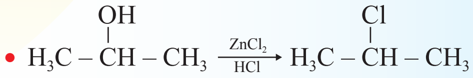
Ethyl chloride and vinyl chloride

- $C_2H_5\text{–}Cl + aq.\ KOH \xrightarrow{\text{Boil}} C_2H_5\text{–}OH + KCl \xrightarrow[\text{AgNO}_3]{\text{HNO}_3} AgCl$
  (Ethyl chloride) (White ppt.)

- $H_2C = CH - Cl + aq.\ KOH \xrightarrow[\text{HNO}_3,\ \text{AgNO}_3]{\text{Boil}} \text{No reaction}$
  Vinyl chloride

n-Propyl alcohol and iso-propyl alcohol

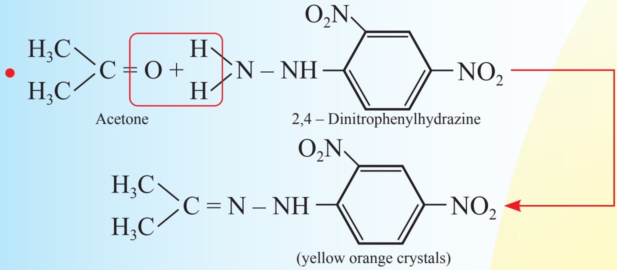
- $CH_3CH_2CH_2OH + HCl \xrightarrow{\text{ZnCl}_2} CH_3CH_2CH_2Cl$
  No cloudiness at room temp.

- 
$H_3C - \underset{|}{\overset{OH}{CH}} - CH_3 \xrightarrow[\text{HCl}]{\text{ZnCl}_2} H_3C - \overset{Cl}{CH} - CH_3$
  Cloudiness within 5 minutes

Ethyl alcohol and methyl alcohol (Iodoform test)

- $CH_3CH_2OH + 4I_2 + 6NaOH \rightarrow \underset{\text{Yellow ppt.}}{CHI_3} + HCOONa$
- $CH_3OH + 4I_2 + 6NaOH \rightarrow$ No yellow ppt.

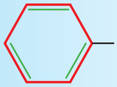
Ethyl alcohol and acetone (2,4 – DNP)



- $C_2H_5OH \xrightarrow{\text{2,4-DNP}}$ No reaction

Phenol and ethyl alcohol (Neutral $FeCl_3$)

- Phenol + Neutral ferric chloride → Violet colouration

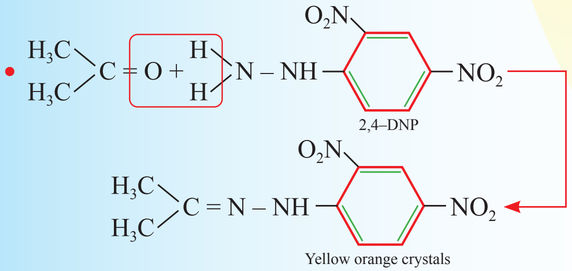
6  $OH + FeCl_3 \rightarrow 3H^+ + \underset{\text{Violet colouration}}{[Fe(OC_6H_5)_6]^{3-}} + 3HCl$

- CH_3CH_2OH + Neutral ferric chloride → No violet colouration

Benzoic acid and phenol ($NaHCO_3$)

- Benzoic acid + Sodium bicarbonate → effervescence
  $C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2 \uparrow + H_2O$
- Phenol + Sodium bicarbonate → No effervescence
  (Phenol is less acidic than benzoic acid)

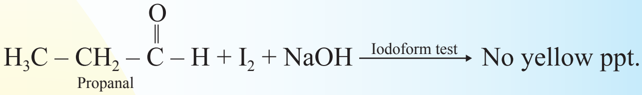
Propanone and propanol (2,4 – DNP)



- Propanol + 2,4–Dinitrophenylhydrazine → No crystals

Ethanal and propanal (Iodoform test)

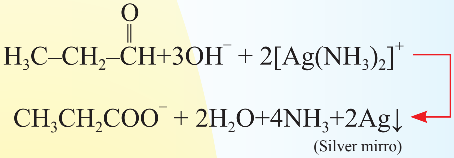
$$\underset{\text{Ethanal}}{H_3C-\overset{O}{\overset{\|}{C}}-H} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3} + HCOONa$$



$$\underset{\text{Propanal}}{H_3C-CH_2-\overset{O}{\overset{\|}{C}}-H} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \text{No yellow ppt.}$$

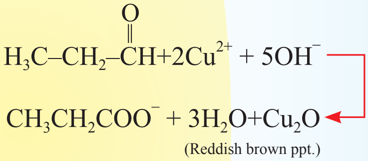
Propanal and propanone (Tollen's and Fehling reagent)

- Propanal + Tollen's reagent → Silver mirror



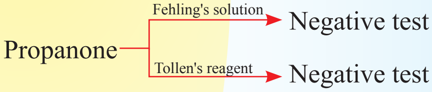
$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}H+3OH^- + 2[Ag(NH_3)_2]^+ \longrightarrow CH_3CH_2COO^- + 2H_2O+4NH_3+\underset{\text{(Silver mirro)}}{2Ag\downarrow}$$

- Propanal + Fehling's solution → Reddish brown precipitate



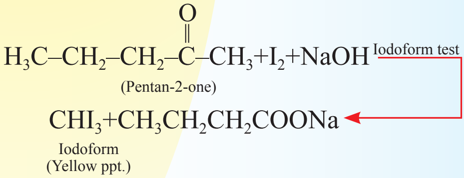
$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}H+2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + 3H_2O+\underset{\text{(Reddish brown ppt.)}}{Cu_2O}$$

- Propanone

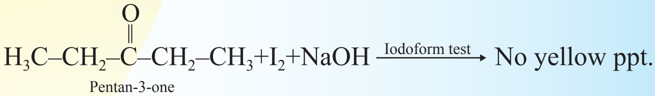


$$\text{Propanone} \xrightarrow{\text{Fehling's solution}} \text{Negative test}$$
$$\text{Propanone} \xrightarrow{\text{Tollen's reagent}} \text{Negative test}$$

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



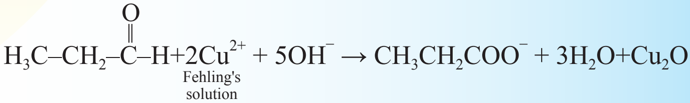
$$\underset{\text{(Pentan-2-one)}}{H_3C-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3}+I_2+NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3}+CH_3CH_2CH_2COONa$$



$$\underset{\text{Pentan-3-one}}{H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3}+I_2+NaOH \xrightarrow{\text{Iodoform test}} \text{No yellow ppt.}$$

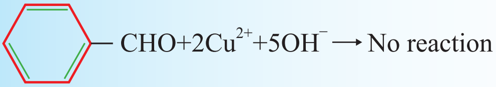
Propanal and benzaldehyde (Fehling solution)

- Propanal + Fehling's solution → Reddish brown precipitate



$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-H+\underset{\substack{\text{Fehling's}\\ \text{solution}}}{2Cu^{2+}} + 5OH^- \rightarrow CH_3CH_2COO^- + 3H_2O+Cu_2O$$

- Benzaldehyde + Fehling's solution → No precipitate



$$C_6H_5\text{–}CHO + 2Cu^{2+} + 5OH^- \longrightarrow \text{No reaction}$$

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

- $\underset{\text{Methanoic acid}}{HCOOH} \xrightarrow{\text{Fehling's solution}} H_2O + CO_3^{2-} + Cu_2O$

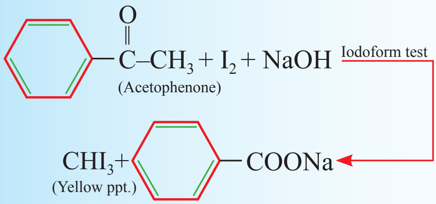
  $\underset{\text{Methanoic acid}}{HCOOH} \xrightarrow{\text{Tollen's reagent}} 2Ag\downarrow + CO_3^{2-} + H_2O$
- Ethanoic acid $\xrightarrow{\text{Fehling's solution}}$ No brown ppt.

  Ethanoic acid $\xrightarrow{\text{Tollen's reagent}}$ No silver mirror

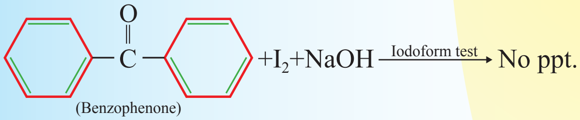
Ethanal and methanal (Iodoform test)

- $\underset{\text{Ethanal}}{CH_3CHO} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3} + HCOONa$
- $\underset{\text{Methanal}}{HCHO} + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Acetophenone and benzophenone (Iodoform test)

- 

$$\underset{\text{(Acetophenone)}}{C_6H_5\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_3} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{(Yellow ppt.)}}{CHI_3} + C_6H_5\text{–}COONa$$

- 

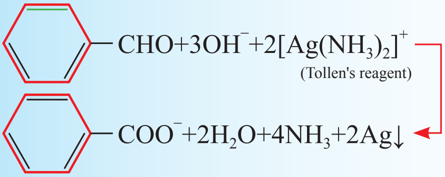
$$\underset{\text{(Benzophenone)}}{C_6H_5\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}C_6H_5} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \text{No ppt.}$$

Benzoic acid and ethylbenzoate

- $C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + \underset{\text{effervescence}}{CO_2\uparrow} + H_2O$
- Ethyl benzoate + Sodium bicarbonate → No effervescence

Benzaldehyde and acetophenone (Tollen's test)

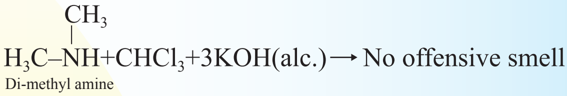
- Benzaldehyde + Tollen's reagent → Silver mirror



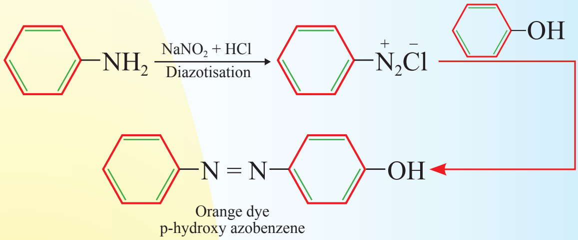
$$C_6H_5\text{–}CHO + 3OH^- + \underset{\text{(Tollen's reagent)}}{2[Ag(NH_3)_2]^+} \longrightarrow C_6H_5\text{–}COO^- + 2H_2O + 4NH_3 + 2Ag\downarrow$$

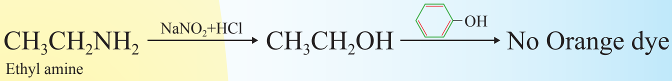
- Acetophenone + Tollen's reagent → No silver mirror

Methyl amine and dimethyl amine (Isocyanide test)

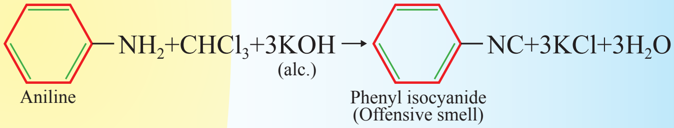
- $\underset{\text{Methyl amine}}{CH_3NH_2} + CHCl_3 + \underset{\text{(alc.)}}{3KOH} \rightarrow \underset{\substack{\text{Methyl isocyanide}\\\text{(Offensive smell)}}}{CH_3NC} + 3KCl + 3H_2O$
- 
  $\underset{\text{Di-methyl amine}}{H_3C\text{–}\overset{\overset{\displaystyle CH_3}{|}}{N}H} + CHCl_3 + 3KOH(alc.) \longrightarrow$ No offensive smell

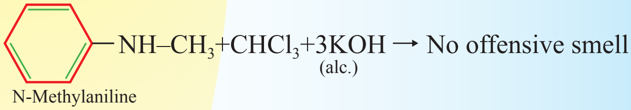
Aniline and ethyl amine (Diazotisation)

- 

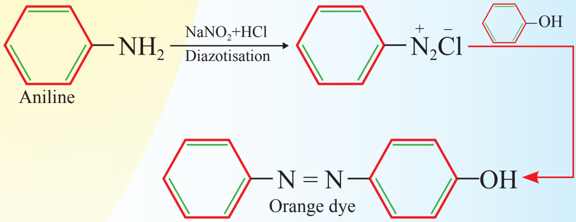
- 

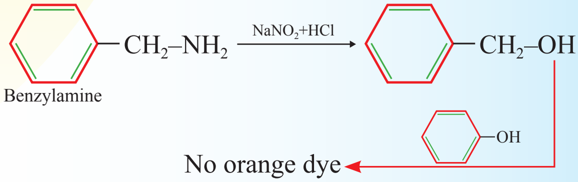
Aniline and N-methylaniline (Isocyanide Test)

- 

- 

Aniline and Benzylamine (Diazotisation + phenol)

- 

- 

Glucose and fructose

- Glucose + $\underset{\text{(Brown colour)}}{Br_2}$ + H_2O → $\underset{\text{(Colourless)}}{\text{Gluconic acid} + 2HBr}$
- Fructose + $\underset{\text{(Brown colour)}}{Br_2}$ + H_2O → $\underset{\text{(no change in colour)}}{\text{Brown colour}}$

Glucose and sucrose

- Glucose + Tollen's reagent → Silver mirror
- Sucrose + Tollen's reagent → No silver mirror

Glucose and starch

- Glucose + Fehling's solution → Red ppt.
- Starch + Fehling's solution → No red ppt.

OR

- Glucose + I_2 solution → No blue colour
- Starch + I_2 solution → Blue colour

❑❑❑

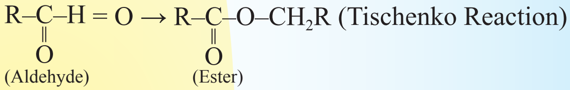
CHAPTER 23

Organic Reagents

1. **Alcoholic KOH**

   R–X → Alkene; Elimination

2. **Aluminium Ethoxide**



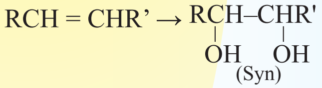
$$\underset{\text{(Aldehyde)}}{R-\underset{\underset{O}{\|}}{C}-H=O} \rightarrow \underset{\text{(Ester)}}{R-\underset{\underset{O}{\|}}{C}-O-CH_2R} \text{ (Tischenko Reaction)}$$

3. **Aqueous KOH/NaOH**

   R–X → ROH

   Nucleophilic substitution reaction also used for Cannizzaro reaction with aldehyde.

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



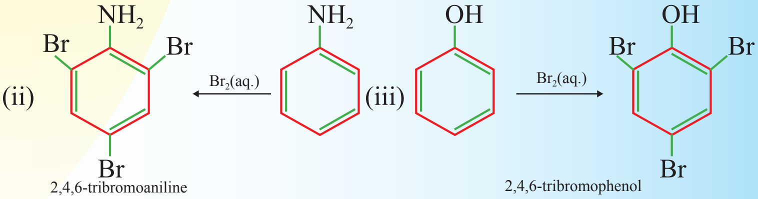
$$RCH=CHR' \rightarrow \underset{\text{(Syn)}}{\underset{OH}{\underset{|}{RCH}}-\underset{OH}{\underset{|}{CHR'}}}$$

   alkene → 1, 2 diol

   (used to detect unsaturation)

5. **Bromine water**

   (i) Used to detect unsaturation;



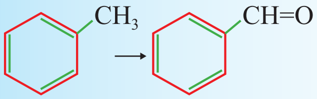
6. **Benedict's solution**

   Used to detect aldehyde group RCHO → RCO_2^- [ketone gives –ve test]

7. $Cu_2Cl_2 + NH_4OH$

Used to Detect Terminal Alkyne
Red Precipitate observed

8. CrO_2Cl_2

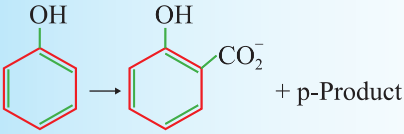


Etard reaction

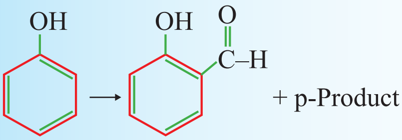
9. CrO_3

(i) $RCH_2OH \rightarrow RCHO$,
(ii) $R_2CHOH \rightarrow R_2C{=}O$
(iii) $R_3COH \rightarrow$ no reaction

10. $CCl_4 + \overset{-}{O}H^{-}$ (Reimer Tiemann)

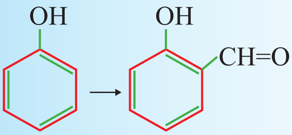


11. $CO + HCl + AlCl_3$



Gatterman koch reaction

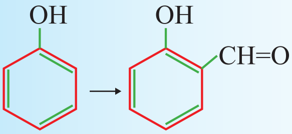
12. $HCN + HCl + AlCl_3$



Gatterman Aldehyde Synthesis

13. $CHCl_3 + KOH$

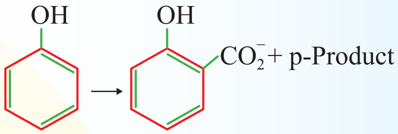
(i)



Reimer Tiemann reaction

(ii) $RNH_2 \rightarrow RNC$ (***Carbyl amine reaction***)
(used to detect 1° amine) (Isocyanide test)

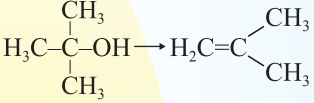
14. $CO_2 + OH^-$ (*high temp. + Pressure*)



Kolbe's reaction

15. Cu/Δ

(i) $RCH_2OH \rightarrow RCHO$,
(ii) $R_2CHOH \rightarrow R_2C{=}O$
(iii)



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \longrightarrow H_2C{=}C(CH_3)_2$$

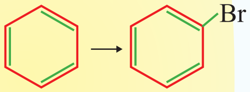
16. 2,4 - D.N.P.

Used to detect carbonyl group (orange ppt. observed)

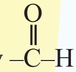
17. DMSO

Polar aprotic solvent: favour S_N2 mechanism.

18. Fe + $Br_2/FeBr_3$



19. Fehling solution



Used to identify $-\overset{\overset{O}{\|}}{C}-H$ group.
PhCHO gives –ve test
Observation: red ppt. of Cu_2O formed

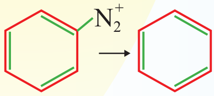
20. Grignard Reagent

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

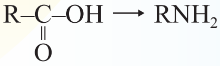
21. $H_2(Pd/CaCO_3)$ Quinoline (Lindlar catalyst)

$R - C \equiv C - R \rightarrow R - CH = CH - R$ (cis)

22. H_3PO_2



23. $HN_3 + H_2SO_4$



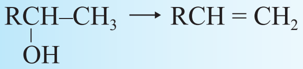
$$R-\underset{\underset{O}{\|}}{C}-OH \longrightarrow RNH_2$$

(Schmidt Reaction)

24. H_3PO_4/Δ

$H_3PO_4 \Rightarrow$ Same as H_2SO_4/Δ

25. H_2SO_4/Δ



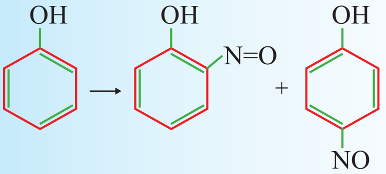
$$\underset{|\atop OH}{RCH}-CH_3 \longrightarrow RCH=CH_2$$

Saytzeff product; C^+ mechanism;
Rearranged alkene can be formed

26. HNO_2 ($NaNO_2 + HCl$)

(i) $RNH_2 \rightarrow R-OH$;
(ii) $PhNH_2 \rightarrow Ph\overset{+}{N}_2$ (0 – 5°C)
(iii) $PhNH_2 \rightarrow PhOH$ (high temperature)

(iv)



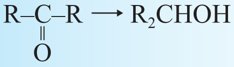
27. HIO_4 (Periodic acid)

$$\underset{|\atop OH}{RCH}-\underset{|\atop OH}{CH}-R \longrightarrow RCH=O + R'CH=O$$

Oxidative cleavage of diol

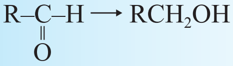
28. H_2(Ni) can reduce

(i)



$$R-\underset{\|\atop O}{C}-R \longrightarrow R_2CHOH$$

(ii)

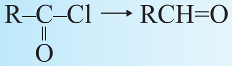


$$R-\underset{\|\atop O}{C}-H \longrightarrow RCH_2OH$$

(iii) $RCN \rightarrow RCH_2NH_2$; $-C\equiv C- \rightarrow -CH_2-CH_2-$,
$-HC=CH- \rightarrow -CH_2-CH_2-$

29. $H_2(Pd/BaSO_4)$

Quinoline



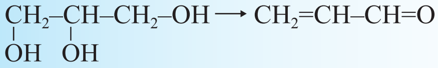
$$R-\underset{\|\atop O}{C}-Cl \longrightarrow RCH=O$$

(Rosenmund reduction)

30. Jones Reagent (CrO_3 + dil. H_2SO_4 + acetone)

(i) $RCH_2OH \rightarrow RCHO$; (ii) $R_2CHOH \rightarrow R_2C=O$

31. $KHSO_4$ Dehydrating Reagent



$$\underset{|\atop OH}{CH_2}-\underset{|\atop OH}{CH}-CH_2-OH \longrightarrow CH_2=CH-CH=O$$

32. $K_2Cr_2O_7/H^+$

(i) $RCH_2OH \rightarrow RCO_2H$; (ii) $R_2CHOH \rightarrow R_2C = O$

33. MnO_2

(i) $CH_3–CH = CH–CH_2–OH \rightarrow CH_3–CH = CH–CH = O$

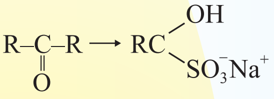
(ii) $PhCH_2OH \rightarrow PhCH = O$

To oxidise allylic/benzylic hydroxyl group into corresponding carbonyl.

34. $NaHCO_3$

$$RCO_2H \xrightarrow{NaH\overset{14}{C}O_3} RCO_2^-Na^+ + \overset{14}{C}O_2\uparrow$$

35. $NaHSO_3$

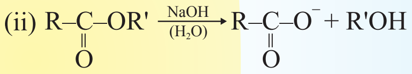


$$R–\underset{\underset{O}{\parallel}}{C}–R \longrightarrow RC\begin{matrix}\diagup OH \\ \diagdown SO_3^-Na^+\end{matrix}$$

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

36. NaOH(aq)

(i) $R–X \rightarrow R–OH$



(ii) $$R–\underset{\underset{O}{\parallel}}{C}–OR' \xrightarrow[(H_2O)]{NaOH} R–\underset{\underset{O}{\parallel}}{C}–O^- + R'OH$$

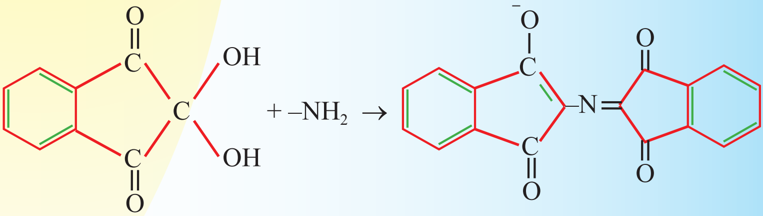
(iii) $HCHO \xrightarrow{OH^-} HCO_2^- + CH_3OH$ (cannizaro)

(iv) $H_3C–CH = O \xrightarrow[\Delta]{OH^-} H_3C–CH = CH–CH = O$

(Aldol condensation)

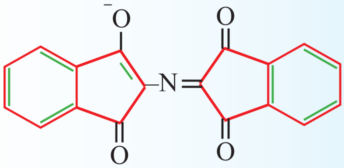
37. Ninhydrin

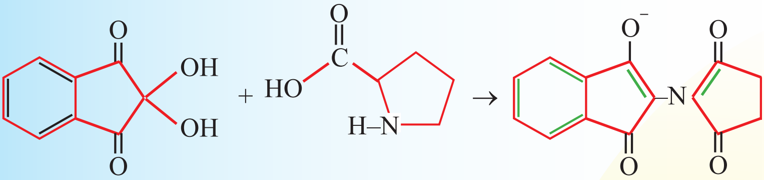
Detection of amino acid



Observation: Purple coloured ion

or

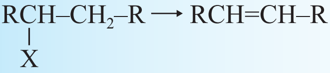




Yellow orange product

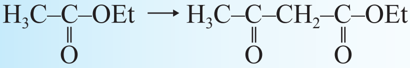
38. NaOR

Strong base:

(i) 

$$\underset{\underset{X}{|}}{RCH}-CH_2-R \longrightarrow RCH{=}CH-R$$

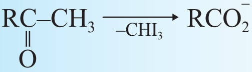
(Saytzeff Product : E_2 elimination)

(ii) 

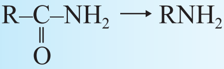
$$H_3C-\underset{\underset{O}{\|}}{C}-OEt \longrightarrow H_3C-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OEt$$

(claisen condensation) (β keto ester)

39. NaOH + X_2 or NaOX

(i) 

$$R\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[-CHI_3]{} RCO_2^-$$ (Haloform reaction)

(ii) 

$$R-\underset{\underset{O}{\|}}{C}-NH_2 \longrightarrow RNH_2$$ (Hoffman Degradation)

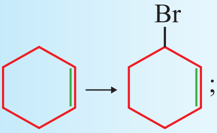
40. NaOH + CaO

$RCO_2H \rightarrow RH$

41. MnO / 300°C

Used for $-CO_2$ & $-H_2O$ in carboxylic acid.

42. NBS

(i) 

(ii) $PhCH_3 \rightarrow PhCH_2-Br$

43. $NaNO_2$ + HCl

$RNH_2 \rightarrow R-OH$

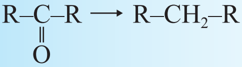
44. $NaNH_2$ in paraffin

Non-terminal Alkyne → Terminal Alkyne
(2-Butyne → 1-Butyne)

45. Na/EtOH

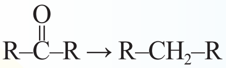
Reduce all except c/c double & triple bond

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



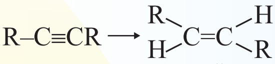
$$R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-CH_2-R$$

47. NH_2-NH_2/OH^- [Wolf Kishner reduction]



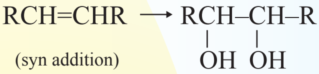
$$R-\overset{\overset{O}{\|}}{C}-R \rightarrow R-CH_2-R$$

48. Na in Liq. NH_3 [Birch reduction]



(trans alkene)

49. $OsO_4 + H_2O$



$$RCH{=}CHR \longrightarrow \underset{OH}{\underset{|}{RCH}}-\underset{OH}{\underset{|}{CH}}-R$$

(syn addition)

50. O_3: $R-CH{=}CH-R \xrightarrow[H_2O\backslash Zn]{O_3} R-CHO+R-CHO$

(Ozonolysis process)

51. Oxirane followed by H^+

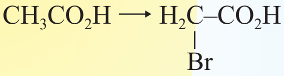
$RMgX \rightarrow RCH_2-CH_2-OH$

52. PCC

(i) $RCH_2OH \rightarrow RCHO$,
(ii) $R_2CHOH \rightarrow R_2C{=}O$
(iii) $R_3COH \rightarrow$ no reaction

(Mild oxidizing reagent)

53. P(red) + Br_2



$$\text{(i) } CH_3CO_2H \longrightarrow H_2\underset{Br}{\underset{|}{C}}-CO_2H \quad \text{(HVZ reaction)}$$

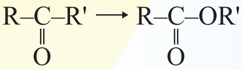
(ii) $ROH \rightarrow R-Br$

54. P (red) + HI

$CH_3CO_2H \rightarrow CH_3-CH_3$
$CH_3CH = O \rightarrow CH_3-CH_3$
$CH_3CH_2OH \rightarrow CH_3-CH_3$

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

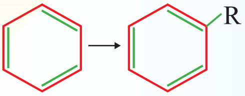
55. Perbenzoic acid [Baeyer Villiger Oxidation]



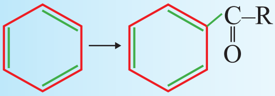
$$R-\underset{O}{\underset{\|}{C}}-R' \longrightarrow R-\underset{O}{\underset{\|}{C}}-OR'$$

R' having more migrating tendency than R

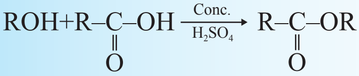
56. RCl + $AlCl_3$ [Friedel craft alkylation]



57. RCOCl + $AlCl_3$ [Friedel craft acylation]



58.



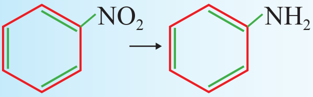
$$ROH + R\text{–}\underset{\overset{\|}{O}}{C}\text{–}OH \xrightarrow[H_2SO_4]{\text{Conc.}} R\text{–}\underset{\overset{\|}{O}}{C}\text{–}OR$$

Ester formed (Esterification reaction)

59. $SnCl_2$ + HCl

(i) $R\text{–}N{=}N\text{–}R' \rightarrow RNH_2 + R'NH_2$

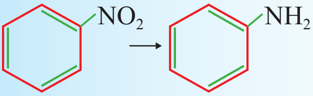
(ii)



(iii) $RCN \rightarrow R\text{–}CH_2NH_2$

60. Sn + HCl

(i)



(ii) $RCN \rightarrow R\text{–}CH_2NH_2$

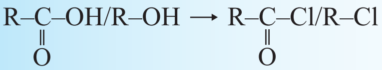
61. Silver salt RCOOAg (Hunsdiecker reaction)

$Br_2/CCl_4/\Delta \rightarrow RBr + CO_2 + AgBr$

62. AgOH/moist Ag_2O; $R_4\overset{+}{N}\overset{-}{X} \rightarrow R_4\overset{+}{N}\overset{-}{O}H$

$Br_2/CCl_4/\Delta \rightarrow RBr + CO_2 + AgBr$

63. $SOCl_2$



$$R\text{–}\underset{\overset{\|}{O}}{C}\text{–}OH/R\text{–}OH \rightarrow R\text{–}\underset{\overset{\|}{O}}{C}\text{–}Cl/R\text{–}Cl$$

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) PhNH–OH gives

65. Benzene sulphonyl chloride

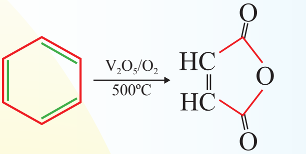
It is used to distinguish and separate (Hinsberg reagent) 1°, 2° and 3° amines.

66. Tetra ethyl lead (TEL)

Used as antiknock compound

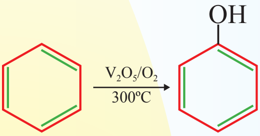
67. V_2O_5

(i)



(Maleic anhydride)

(ii)



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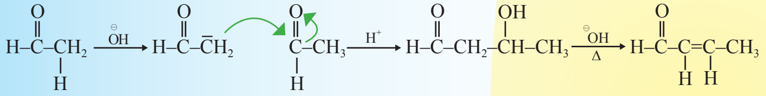
CHAPTER 24

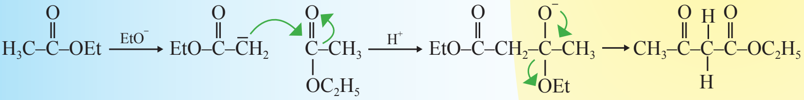
Organic Name Reactions

Aldol Condensation



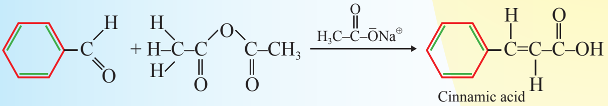
$$H-\underset{H}{\underset{|}{\overset{O}{\overset{\|}{C}}}}-CH_2 \xrightarrow{\overset{\ominus}{O}H} H-\overset{O}{\overset{\|}{C}}-\overset{-}{C}H_2 \quad \underset{H}{\underset{|}{\overset{O}{\overset{\|}{C}}}}-CH_3 \xrightarrow{H^+} H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{C}}H-CH_3 \xrightarrow[\Delta]{\overset{\ominus}{O}H} H-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-CH_3$$

Claisen Condensation

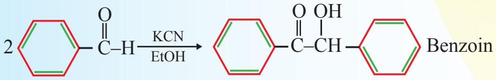


$$H_3C-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{EtO^-} EtO-\overset{O}{\overset{\|}{C}}-\overset{-}{C}H_2 \quad \underset{OC_2H_5}{\underset{|}{\overset{O}{\overset{\|}{C}}}}-CH_3 \xrightarrow{H^+} EtO-\overset{O}{\overset{\|}{C}}-CH_2-\underset{OEt}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

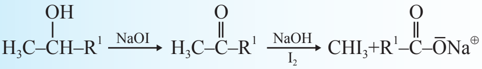
Perkin Condensation



Benzoin Condensation

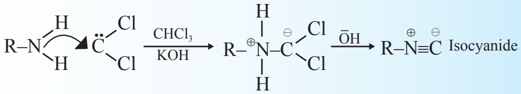


Haloform Reaction

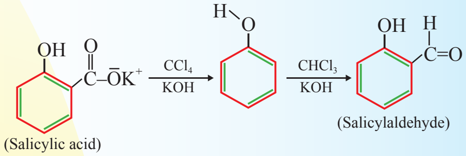


$$H_3C-\overset{OH}{\overset{|}{C}}H-R^1 \xrightarrow{NaOI} H_3C-\overset{O}{\overset{\|}{C}}-R^1 \xrightarrow[I_2]{NaOH} CHI_3+R^1-\overset{O}{\overset{\|}{C}}-\bar{O}Na^{\oplus}$$

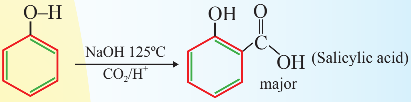
Carbylamine Test



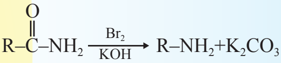
Reimer Tiemman Reaction



Kolbe's Schimdt Reaction

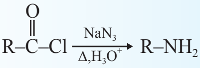


Hoffmann Bromamide Degradation



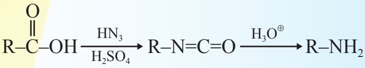
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[KOH]{Br_2} R-NH_2+K_2CO_3$$

Curtius Reaction



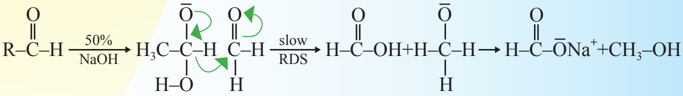
$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\Delta, H_3O^+]{NaN_3} R-NH_2$$

Schimdt Reaction

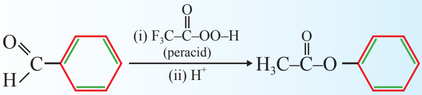


$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_2SO_4]{HN_3} R-N=C=O \xrightarrow{H_3O^\oplus} R-NH_2$$

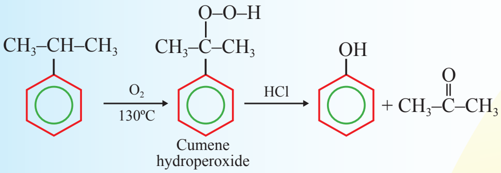
Cannizzaro Reaction



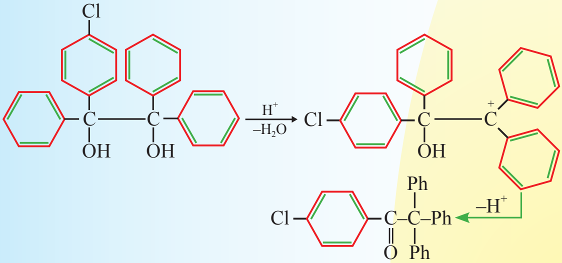
Bayer villiger oxidation



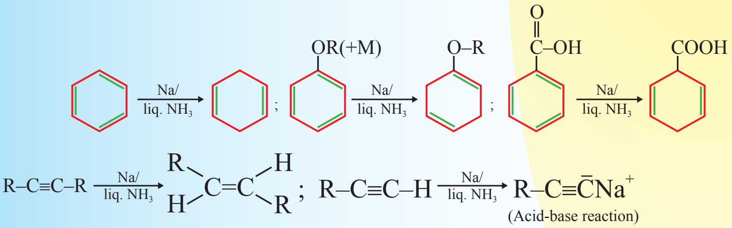
Cumene



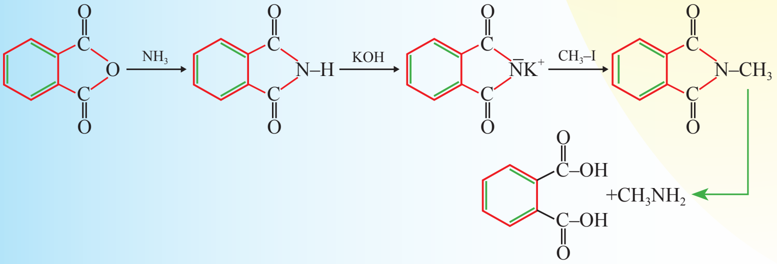
Pinacol-Pincolone rearrangement

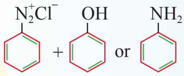
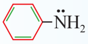
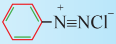
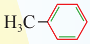
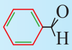
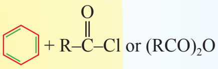


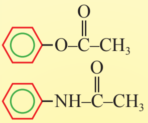
Birch Reduction



Gabriel Synthesis

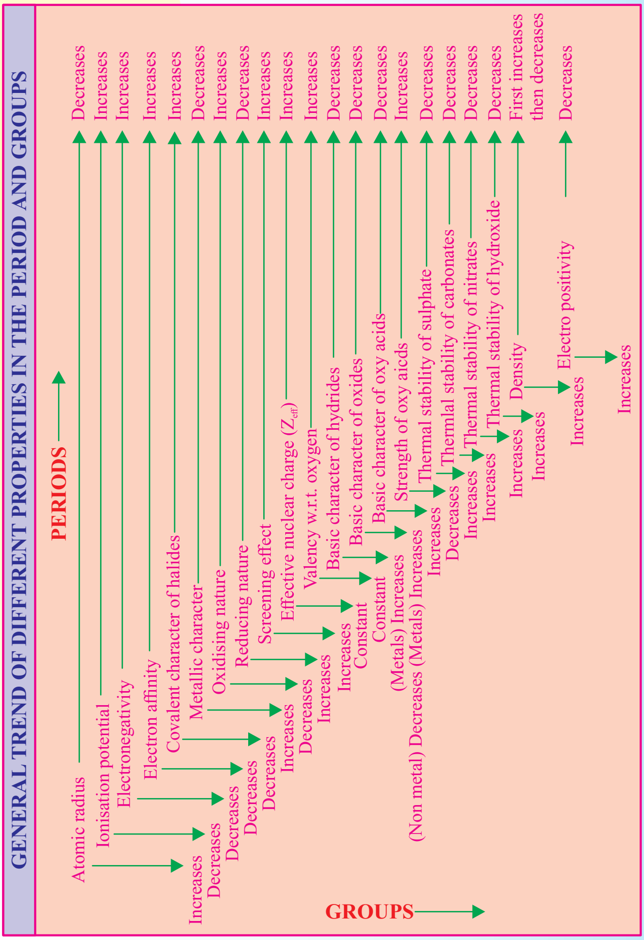


Name	Reactant	Reagent	Product
Clemmensen Reduction	Aldehyde & Ketone	Zn-Hg/conc. HCl	Alkane
Coupling Reaction		NaOH (phenol) HCl (Aniline)	Azo Dye (Detectionof OH or NH_2 gr)
Diazotization		$NaNO_2 + HCl$ $(0^{\circ} - 5^{\circ}C)$	
Etard reaction		CrO_2Cl_2/CS_2	 (Benzalde hyde)
Fitting Reaction	Halo benzene	Na/Dry ether	Diphenyl
Friedel Craft alkylation	 + R–X	Anhydrous $AlCl_3$	Alkyl Benzene
Friedel Craft acylation	 $+ R-\overset{O}{\overset{\|}{C}}-Cl$ or $(RCO)_2O$	Anhydrous $AlCl_3$	Acyl Benzene
Gattermann aldehyde synthesis	C_6H_6	$HCN+HCl/ZnCl_2/$ H_3O^+	Benzaldehyde
Gattermann-Koch reaction	C_6H_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	$HgCl_2/\Delta$	$CH_3CH_2-N=C=S+HgS$ (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_2H_5OH	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, 200–300ºC	Alkane
Sandmeyer reaction	$C_6H_5\overset{+}{N_2}Cl^-$	CuCl/HCl or CuBr/HBr or CuCN/KCN, heat	Halo or cyanobenzene
Gattermann Reaction	$C_6H_5\overset{+}{N_2}Cl^-$	Cu/HX(HBr/HCl)	Halobenzene
Schotten-Baumann reaction	(phenol or aniline or alcohol)	NaOH + C_6H_5COCl	benzolytated 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

CHAPTER 25

Periodic Properties



GENERAL TREND OF DIFFERENT PROPERTIES IN THE PERIOD AND GROUPS

	PERIODS →	GROUPS →
Atomic radius	Decreases	Increases
Ionisation potential	Increases	Decreases
Electronegativity	Increases	Decreases
Electron affinity	Increases	Decreases
Covalent character of halides	Increases	Decreases
Metallic character	Decreases	Increases
Oxidising nature	Increases	Decreases
Reducing nature	Decreases	Increases
Screening effect	Increases	Increases
Effective nuclear charge (Z_{eff})	Increases	Constant
Valency w.r.t. oxygen	Increases	Constant
Basic character of hydrides	Decreases	(Metals) Increases
Basic character of oxides	Decreases	(Non metal) Decreases (Metals) Increases
Basic character of oxy acids	Decreases	Increases
Strength of oxy aicds	Increases	Decreases
Thermal stability of sulphate	Decreases	Increases
Thermlal stability of carbonates	Decreases	Increases
Thermal stability of nitrates	Decreases	Increases
Thermal stability of hydroxide	Decreases	Increases
Density	First increases then decreases	Increases
Electro positivity	Decreases	Increases

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 definations 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 $\propto$ Number of shells

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

Periodic Trends:

(1) Generally increases on moving down the group.

(2) Generally decrease when we are moving left to right in the period.

NOTES

Atomic radius of Al > Ga : Due to poor sheilding of 3d subshell electron.

Atomic radius of 4d ≈ 5d series element due lanthanide constraction.

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:

$$A^{+} \longleftarrow A \longrightarrow A^{-}$$

Z_{eff}	$A^{+} > A > A^{-}$
Ionic radius	$A^{+} < A < A^{-}$

Factors Affecting Ionic Radius

(+) charge ↑	ionic radius ↓
(–) charge ↑	ionic radius ↑
Z_{eff} ↑	ionic radius ↓
n ↑	ionic radius ↑

⇒ In isoelectronic species (+) charge ↑ Ionic radius ↓
(–) charge ↑ tonic radius ↑

eg.: $N^{3-} > O^{2-} > F^{-} > Na^{+} > Mg^{2+} > Al^{3+}$

$K^{+} > Li^{+} > Mg^{2+} > Al^{3+}$

IONIZATION ENERGY

Energy required to remove to loosely bonded e^{-} from isolated gaseous atom.

Successive I.E.

$I.E_1$, $I.E_2$, ... combinedly termed as successive I.E.

$$A_{(g)} \xrightarrow{IE_1} A^{+}_{(g)} \xrightarrow{IE_2} A^{2+}_{(g)} \xrightarrow{IE_3} A^{3+}_{(g)} \xrightarrow{IE_3}$$

$IE_1 < IE_2 < IE_3$ ......

Factors Affecting

(1) $IE \propto Z_{eff}$

(2) $IE \propto \dfrac{1}{\text{size}}$

(2) $IE \propto$ (+) charge,

(4) $IE \propto \dfrac{1}{(-)\,\text{charge}}$

(5) half filled and full filled configration (allected 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)

$ns^1 < np^1 < ns^2 < np^2 < np^4 < np^3 < np^5 < np^6$

NOTES

after 4th period (Ionization Energy)

$ns^1 < ns^2 < np^1 < np^2 < np^3 < np^4 < np^5 < np^6$

Al < Ga (Poor sheilding of 3d sutshell e^-)

T1 > ln
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.

Sc > Y > La, Ag < Cu < Au, Cd < Zn < Hg

Application of Ionization Energy

IE↑ Metallic Character ↓
IE↑ Electropositive Character ↓
IE↑ Reducing Property ↓

NOTES

Number of valence e^- = highest jump in successive IE

eg.: $IE_1 < IE_2 < IE_3 <<< IE_4 < IE_5$

Highest jump between IE_3 & IE_4 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

$$A_{(g)} \xrightarrow{EA_1} A^-_{(g)} \xrightarrow{EA_2} A^{2-}_{(g)} \xrightarrow{EA_3} A^{3-}_{(g)}$$

EA_1 is generally exothermic except N, Be, Mg and Noble gas

EA_2, EA_3 ..... always endothemic

Factors Affecting

(1) $EA \propto Z_{eff}$

(2) $EA \propto \frac{1}{\text{size}}$

(3) Nature of subshell

(4) hall and full filled

Periodic Trend

(1) Generally decreases on moving down the group

(2) Generally increase when moving left to right in the period.

NOTES

IIIrd period element having greater EA than IInd period element except alkali metal.

$O < Te < Se < S$, $I < Br < F < CI$

NOTES

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

Electronegativity

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

Factors Affecting

(1) $EN \propto Z_{eff}$

(2) $EN \propto \frac{1}{\text{size}}$

(3) $EN \propto \frac{1}{(-)\text{ charge}}$

(4) $EN \propto (+)$ charge,

(5) $EN \propto \%$ s-characters 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^{+}

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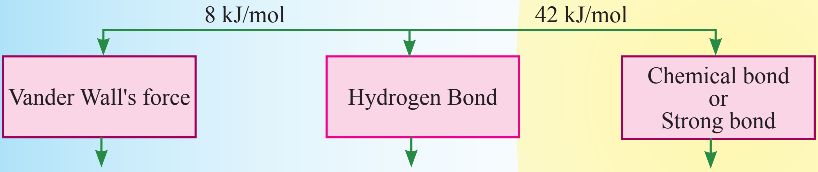
CHAPTER 26

Chemical Bonding

CHEMICAL BOND

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

It is always exothermic process.



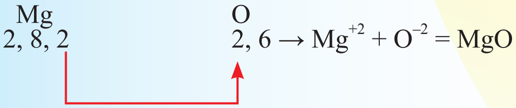
1. Dipole-Dipole (Keesome)
2. Dipole-induce dipole (Debye)
3. Instantaneous diple-induce dipole
4. Ion-dipole
5. Ion-induced dipole

1. Intermolecular hydrogen bond
2. Intramolecular hydrogen bond

1. Ionic bond
2. Covalent bond
3. Co-ordinate bond
4. Metallic bond

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.



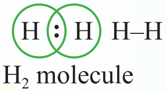
$$\underset{2,\,8,\,2}{\text{Mg}} \qquad \underset{2,\,6}{\text{O}} \rightarrow Mg^{+2} + O^{-2} = MgO$$

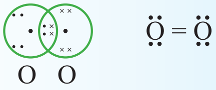
electrovalency of Mg = 2

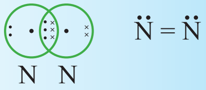
electrovalency of O = 2

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)



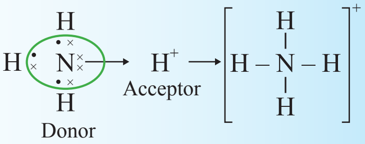




COORDINATE BOND (DATIVE BOND)

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.

(i) NH_4^+ (ammonium ion)



(ii) $F_3B + :NH_3 \rightarrow (F_3B \leftarrow NH_3)$

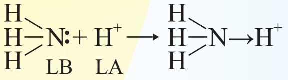
EXCEPTION OF OCTET RULE		
(a) electron deficient Central atom: No. of electron < 8 BeH_2 BF_3, BCl_3, BBr_3, BI_3 $AlCl_3, AlBr_3, AlI_3$	**(b)** electron rich Central atom: No. of electron > 8 PCl_5, IF_7 SF_6, XeF_2	**(c)** odd electron species central atom : has odd electron NO, NO_2, ClO_2, ClO_3

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.

Eg.



$$H_3N: + H^+ \longrightarrow H_3N\rightarrow H^+$$

Similarly

$$H_2O + H^+ \longrightarrow H_3O^+$$
$$BF_3 + F^- \longrightarrow BF_4^-$$
$$NH_3 + BF_3 \longrightarrow F_3B.NH_3$$

- Donor atom follow octet rule.

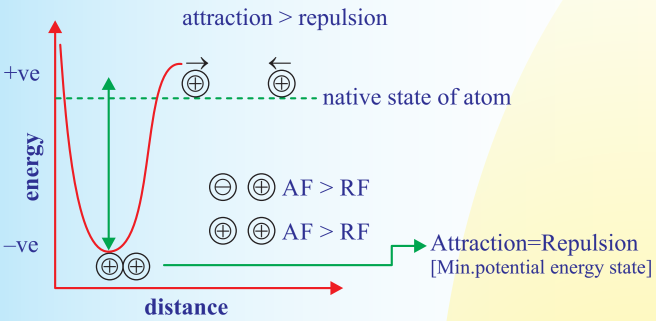
MODERN APPROACH OF COVALENT BOND

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.

$$\text{Stability} \propto \frac{1}{\text{Potential energy}}$$



- 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 < Nucleus
Shell - subshell - orbital - electron - cloud

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 ∝ extent of overlapping.

1. Nature of Orbitals

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

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

$$\boxed{1\text{-}1 > 1\text{-}2 > 2\text{-}2 > 2\text{-}3}$$

- **Exception:** $Cl_2 > Br_2 > F_2 > I_2$ due to
  O—O < S—S lp-lp
  N—N < 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

Possibler Combination & Strength of Overlapping

s-s < s-p < p-p

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

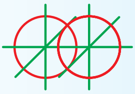
2s - 2s < 2s - 2p < 2p - 2p	sub-shell factor
1s - 1s > 1s - 2s > 1s - 3s	shell factor

2. Pattern of Overlapping

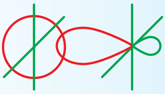
(a) Axial overlapping:

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

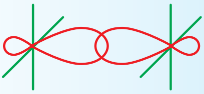
s-s



s-p



p-p

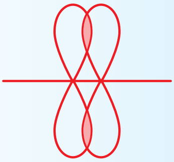


(b) Co-lateral overlapping

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

Weak bond

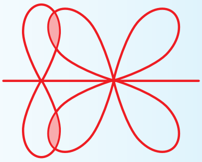
p-p overlapping



Internuclear axis

p_π-p_π
pi-bond

p-d overlapping



p_π-d_π
pi-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^3d	Triangular bipyramidal	PCl_5
5.	one s + three p + two d	6; sp^3d^2	Octahedral	SF_6
6.	one s + three p + three d	7; sp^3d^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^{-1}, SO_4^{-2}, $AlCl_4^-$,
(b) sp^3-hybridisation	3	1	Pyramidal	NH_3, PF_3, ClO_3^-, H_3O^+, PCl_3, XeO_3, $N(CH_3)_3$, CH_3^-
(c) sp^3-hybridisation	2	2	V-shape Angular	H_2O, H_2S, NH_2^-, OF_2, Cl_2O_2, SF_2, I_3^+
4. (a) sp^3d-hybridisation	5	–	Trigonal bipyramidal	PCl_5, SOF_4, AsF_5
(b) sp^3d-hybridisation	4	1	See-Saw, folded square distorted tetrahedral	SF_4, PF_4^-, AsF_4^- SbF_4^-, XeO_2F_2
(c) sp^3d-hybridisation	3	2	almost T-shape	ClF_3, ICl_3
(d) sp^3d-hybridisation	2	3	Linear	I_3^-, Br_3^-, ICl_2^-, XeF_2
5. (a) sp^3d^2-hybridisation	6	–	Square bipyramidal/ octahedral	PCl_6^-, SF_6
(b) sp^3d^2-hybridisation	5	1	Square pyramidal/ distorted octahedral	$XeOF_4$, ClF_5, SF_5^-,
(c) sp^3d^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

$\boxed{\vec{\mu} = q \times d}$ debye = esu-cm

$1D = 10^{-18}$ esu.cm

(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 $\Delta EN = 0 \rightarrow \vec{\mu} = 0 \rightarrow$ Non-polar.

H_2, F_2, Cl_2, N_2 etc.

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

$NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$

$NH_3 > SbH_3 > AsH_3 > PH_3$

$H_2O > H_2S$

$CH_3Cl > CH_3F > CH_3Br > CH_3I$

$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

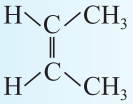
Applications

Predict shape and polarity of molecule

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

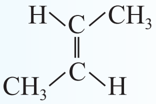
Unsymmetrical geometry → $\mu \neq 0$ → polar

Distinguish between cis & transform



maleic acid

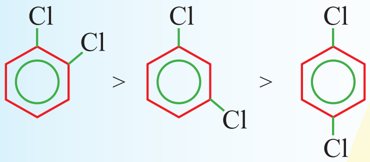
$\mu \neq 0$



fumaric acid

$\mu = 0$

Dipole moment in Aromatic Compounds



Orthodichloro benzene

Metadichloro benzene

Paradichloro benzene

$$\mu \propto \frac{1}{\text{bond angle}}$$

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 $(HF)_6$, 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 (densile 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:

(i) Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.

(ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.

(iii) 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.**

(iv) 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.

(v) 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.

$\psi_{MO} = \psi_A + \psi_B$ (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:

$\psi^*_{MO} = \psi_A - \psi_B$ (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 N_2 (molecule having $\leq$ 14 electrons)

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$

Molecular orbital energy diagram for O_2 and F_2 (molecule having > 14 electrons)

$\sigma_{1s} < \sigma^*_{1s} \,; < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$

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 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 filed), 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 $(HF)_6$, 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	½	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	½	paramagnetic
6.	6	4	2	1	diamagnetic
7.	7	4	3	½	paramagnetic
8.	8	4	4	0	does not exist
9.	9	5	4	½	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

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

BONDING PARAMETER

1. Bond length: Internuclear distance

Factor affecting Bond length

(i) Atomic size: bond length ∝ size```` [No. of shell]

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

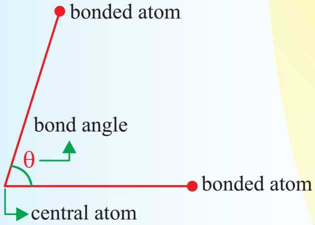
$$\boxed{d_{A-B} = r_A + r_B - 0.09 \times \Delta EN\,\text{Å}}$$

(iii) Bond order: Bond length $\propto \frac{1}{B.O.}$

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

Bond Angle

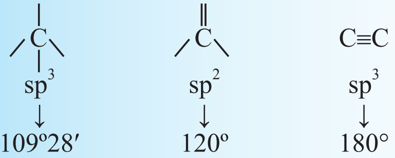
Angle between two adjacent bond is known as bond angle.



FACTORS AFFECTING BOND ANGLE

(i) Hybridisation

Bond angle ∝ % age of s-character



(ii) No. of lp/bp

[when hybridisation is same]

Bond angle $\propto \frac{1}{lp}$ Eg.: $CH_4 > \ddot{N}H_3 > H_2\ddot{O}:$

(iii) Type of Central atom: Applicable when:

- hybridisation same
- No. of lp/bp same

Bond angle ∝ EN of central atom.

Eg. $NH_3 > PH_3 > AsH_3 > SbH_3$

(iv) Type of bonded atom: Applicable when:

- hybridisation - same
- No. of lp/bp - same
- Central atom - same

Bond angle ∝ size of bonded species

Eg. $OF_2 < OCl_2 < OBr_2 < OI_2$

NOTES

Regular geometry / same hybridisation / bond angle same $BF_3 = BCl_3 = BBr_3 = BI_3$

Ionic Bond

Extreme polar covalent bond is an Ionic Bond.

Therefore Ionic Bond ΔEN - Must be higher - one specie - lower EN - metal one specie - higher EN - non metal

Eg. NaCl, KF

Formation of Ionic Bond takes place in following step.

$$\underset{\text{Solid}}{\text{Metal (M)}} \xrightarrow[\Delta H = +ve \\ \text{S.E.}]{\text{Sublimation}} M(g) \xrightarrow[\Delta H = +ve \\ \text{I.E.}]{\text{Ionisation}} M^+_{(g)}\,; \quad \underset{\text{Non metal molecule}}{X_2} \xrightarrow[\Delta H = +ve \\ \text{B.D.E.}]{\text{Dissociation}}$$

$$X \xrightarrow[\Delta H = -ve \\ \text{electron gain enthalpy}]{+e^-} X^-_{(g)} \qquad M^+_{(g)} + X^-_{(g)} \xrightarrow[\Delta H = -ve \\ \text{lattice energy}]{} MX_{(solid)}$$

$\Delta H_{formation} = S.E. + I.E. + \frac{1}{2}BDE + \Delta H_{eg} + U$

bond formation is always an exothermic process.

$\Delta H_{formation} = -ve$

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

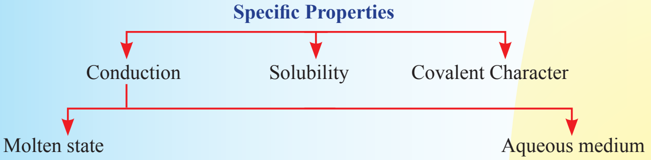
General Properties

Hard, Solid, Brittle (strong electrostatic attraction between ions)

Non directional nature (ionic compound do not exhibit stereo isomerism)

Higher Melting Point / Boiling Point

Isomorphism: $MgSO_4 . 7H_2O$; $ZnSO_4 . 7H_2O$; $FeSO_4 . 7H_2O$



Molten state

Ionic conduction $\propto \dfrac{1}{\text{Ionic radius}}$

Eg. : LiCl, NaCl, KCl, RbCl, CsCl
Ionic Radius: $Li^+ <<< Cs^+$
Conductance: CsCl < RbCl < KCl < NaCl < LiCl

Aqueous medium

Ionic mobility $\propto \dfrac{1}{\text{Ionic radius}}$

Hyd. radius: $Cs^+ <<< Li^+(aq)$
conductance: LiCl < NaCl < KCl < RbCl, CsCl

COVALENT CHARACTER / FAJAN'S RULE

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

Polarisibility of anion $\propto$ size of anion $\propto$ 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) $\overset{+2}{Cr}O < \overset{+3}{Cr_2}O_3 < \overset{+6}{Cr}O_3$ Covalent character ↑

(ii) $\overset{+2}{S}F_2 < \overset{+4}{S}F_4 < \overset{+6}{S}F_6$ Covalent character ↑

(iii) $Li\overset{-1}{F} < Li_2\overset{-2}{O} < Li_3\overset{-3}{N}$ Covalent character ↑ (anion charge↑)

(2) Polarisation $\propto \dfrac{\text{size of anion}}{\text{size of cation}}$

Eg. (i) LiF < LiCl < LiBr < LiI anion size ↑
polarisability ↑
covalent character ↑

(ii) $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ cation size ↑
polarisation ↓
covalent character ↑

SOLUBILITY

For s-block

Same group cation

Lattice Energy / Hydration Energy

(i) $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$, $BeCO_3$

(ii) $Be(OH)_2$, $Sr(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$

(iii) $BaSO_4$, $SrSO_4$, $CaSO_4$, $MgSO_4$, $BeSO_4$

(iv) Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3

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

(vi) LiF, LiCl, LiBr, LiI

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

(viii) BaF_2, SrF_2, MgF_2, CaF_2, BeF_2

(ix) CaF_2, $CaCl_2$, $CaBr_2$, Cal_2

$$\left.\begin{array}{l}\text{(x) AgI, AgBr, AgCl, AgF}\\ \text{(xi) PbO}_2\text{, CdI}_2\text{, RbI}\end{array}\right] \text{solubility} \propto \frac{1}{\text{covalent char.}}$$

For all solubility $\propto \dfrac{1}{\textbf{covalent char.}}$

solubility in org. solvent $\propto$ **cov. char** $\propto \dfrac{1}{\textbf{ionic char.}}$

[CCl_4, benzene, ether, alcohol, acetone]

Eg. (i) $PbF_2 > PbCl_2 > PbBr_2 > PbI_2$

(Anion size↑, cov. char.↑, solubility ↓)

(ii) $Fe^{+2}(OH)_2 > Fe^{+3}(OH)_3$

(+) charge↑, PP↑, CC↑, solubility ↓

(iii) $ZnCl_2 > CdCl_2 > HgCl_2$

Z_{eff}↑, PP↑, CC↑, solubility ↓

(iv) $Na_2SO_4 > MgSO_4$

(+) charge↑, PP↑, CC↑, solubility ↓

(v) $ZnCl_2 > CdCl_2 > HgCl_2$

Z_{eff}↑, PP↑, CC↑, solubility ↓

(vi) NaCl > CuCl

PP↑, CC↑, solubility ↓

(vii) AgF > AgCl > AgBr > AgI

Anionic Size↑, PP↑, CC↑, solubility ↓

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)

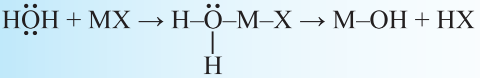
SILICATES			
Silicates	**Sharing of O-atom/Basic Tetrahedral unit**	**Contribution of O-atom/Basic Tetrahedral unit**	**General formula**
Ortho	0	4	SiO_4^{4-}
Pyro	1	3.5	$Si_2O_7^{6-}$
Cyclic	2	3	$(SiO_3)_n^{2n-}$
Simple chain (pyroxene)	2	3	$(SiO_3)_n^{2n-}$
Double chain (Amphibole)	(3,2) avg. = 2.5	$\frac{11}{4} = \left(\frac{5.5}{2}\right)$	$(Si_4O_{11})_n^{6n-}$
2D or (Sheet)	3	2.5	$(Si_2O_5)_n^{2n-}$
3D	4	2	$(SiO_2)_n$

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.
- 

$$\underset{\text{molecule}}{H\ddot{\underset{..}{O}}H + MX} \rightarrow \underset{\text{Intermediate}}{H\text{–}\underset{\underset{H}{|}}{\ddot{O}}\text{–}M\text{–}X} \rightarrow \underset{\text{Product}}{M\text{–}OH + HX}$$

Extent of Hydrolysis ∝ Covalent Character

$BeCl_2 + 2HOH \rightarrow Be(OH)_2 + 2HCl$

$BCl_3 + 3HOH \rightarrow B(OH)_3 + 3HCl$

$AlCl_3 + 3HOH \rightarrow Al(OH)_3 + 3HCl$

$SiCl_4 + 4HOH \rightarrow Si(OH)_4 + 4HCl$

$SF_6 + H_2O \rightarrow$ No hydrolysis due to crowding

$CCl_4 + HOH \xrightarrow[\text{conditions}]{\text{ordinary}}$ No hydrolysis

$BF_3 + 3HOH \rightarrow B(OH)_3 + 3HF$

$3BF_3 + 3HF \rightarrow 3H^+ [BF_4]^-$

$4BF_3 + 3H_2O \rightarrow 3H[BF_4]$

(partially hydrolysis)

Similarly

$SiF_4 + 4HOH \rightarrow Si(OH)_4 + 4HF$

$2SiF_4 + 4HF \rightarrow H_2^+ [SiF_6]^{2-}$

hydrolysis followed by
Lewis acid-base reaction.

15th Group Halides

$NF_3 + HOH \xrightarrow[\text{conditions}]{\text{ordinary}}$ No hydrolysis

$NCl_3 + HOH \rightarrow NH_3 + 3HOCl$

$PCl_3 + HOH \rightarrow H_3PO_3 + 3HCl$

$AsCl_3 + HOH \rightarrow As(OH)_3 + 3HCl$

$SbCl_3 + HOH \rightarrow SbOCl + 2HCl$
(partial hydrolysis)

$BiCl_3 + HOH \rightarrow BiOCl + 2HCl$
(partial hydrolysis)

$PCl_5 + HOH \rightarrow \underset{\text{partial}}{POCl_3} \rightarrow \underset{\text{completely}}{H_3PO_4}$

Hydrolysis of Higher Covalent Character Containing Salt

$Be_2C + 4HOH \rightarrow 2Be(OH)_2 + CH_4$

$Mg_2C_3 + 4HOH \rightarrow 2Mg(OH)_2 + C_3H_4$

$CaC_2 + 2HOH \rightarrow Ca(OH)_2 + C_2H_2$

$Al_4C_3 + 12HOH \rightarrow 4Al(OH)_3 + 3CH_4$

$Mg_3N_2 + 6HOH \rightarrow 3Mg(OH)_2 + 2NH_3$

$AlN + 3HOH \rightarrow Al(OH)_3 + NH_3$

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

$LiH + HOH \rightarrow LiOH + H_2$

$CaH_2 + 2HOH \rightarrow Ca(OH)_2 + H_2$

Hydrolysis of Interhalogen Compounds

$AX + HOH \rightarrow HX + HOA$

$AX_3 + HOH \rightarrow 3HX + HAO_2$

$AX_5 + HOH \rightarrow 5HX + HAO_3$

$AX_7 + HOH \rightarrow 7HX + HAO_4$

HX Hydrohalic acid

HOA, HAO_2, HAO_3, HAO_4
oxyacid of halogen

Some Specific Hydrolysis

$XeF_2 \xrightarrow{HOH} Xe + 2HF + O_2$

$6XeF_4 \xrightarrow{HOH} 4Xe + 2XeO_3 + 24HF + 3O_2$

$$XeF_6 \xrightarrow{HOH} \underset{\text{partial}}{2HF + XeOF_4} \xrightarrow{HOH} \underset{\text{partial}}{2HF + XeO_2F_2} \xrightarrow{HOH} \underset{\text{complete}}{2HF + XeO_3}$$

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^-, $O(SiH_3)$, $N(SiH_3)_2$, SiH_5O^-, etc.

Application of Back Bonding

Lewis acid character:

$BF_3 < BCl_3 < BBr_3 < BI_3$

$BeF_2 < BeCl_2 < BeBr_2 < BeI_2$

$SiF_4 > SiCl_4 > SiBr_4 > SiI_4$

Lewis basic character:

$N(CH_3)_3 > N(SiH_3)_3$

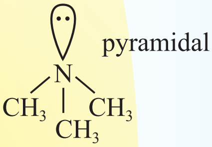
$O(CH_3)_3 > O(SiH_3)_3$

NOTES

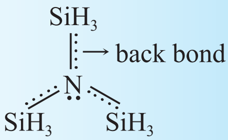
Due to back bonding $\underline{B}_3N_3H_6$, $(\underline{B}O_2)_3^{3-}$, $\underline{N}(SiH_3)_3$ is planar around under lined atom.

Few more examples of Back Bonding

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



No back bonding due to
no vacant orbital in carbon.

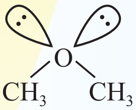


Trigonal Planar

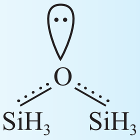
2. Lewis base strength

$\ddot{N}(CH_3)_3 > \underset{\text{lp involve in back bonding}}{\underline{\ddot{N}(SiH_3)_3}}$

3. Bond angle of $(CH_3)_2O$ is very less than $(SiH_3)_2O$



No back bonding
C : No vacant orbital



back bond effect of lp ↓
bond angle ↑

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_2Cl_4	(3c-4e)	sp^2
$(BeCl_2)_n$	(3c-4e)	sp^3
Al_2Cl_6	(3c-4e)	sp^3
I_2Cl_6	(3c-4e)	sp^3d^2
B_2H_6	(3c-2e)	sp^3
Be_2H_4	(3c-2e)	sp^2
$(BeH_2)_n$	(3c-2e)	sp^3
$(AlH_3)_n$	(3c-2e)	sp^3d^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
$^{\bullet}CH_3$	sp^2	Trigonal planar	Para
$^{\bullet}CH_3/^{\bullet}CHF_2/CH_2F$	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. $CO_2 + HOH \rightarrow H_2CO_3$ or $OC(OH)_2$

Here: $CO_2 \rightarrow$ Non metal oxide - Anhydride of carbonic acid
$OC(OH)_2 \rightarrow$ Oxyacid

- $NO_2 \rightarrow$ Mixed anhydride
- it gives $\rightarrow HNO_2$ & HNO_3

Oxide		Acid		
N_2O_3	→	HNO_2	–	Nitrous acid
N_2O_5	→	HNO_3	–	Nitric acid

- P_4O_{10} → H_3PO_4 – Phosphoric acid
- SO_2 → H_2SO_3 – Sulphurous acid
- SO_3 → H_2SO_4 – Sulphuric acid
- Cl_2O_7 → $HClO_4$ – Perchloric acid
- Oxyacids of different elements

Order of acidic strength

$H_3PO_2 > H_3PO_3 > H_3PO_4$

Reducing nature

$H_3PO_2 > H_3PO_3 > H_3PO_4$

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 aicd 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) - $H_2S_2O_8$ (Peroxide bond)
6. Pyrosulphurous acid - $H_2S_2O_5$ - (S-S linkage)
7. Pyrosulphuric acid - $H_2S_2O_7$ (S-O-S linkage)
8. Thionus acid - $H_2S_2O_4$
9. Thionic acid - $H_2S_2O_6$
10. Polythionus acid - $H_2(S)_nO_4$ (S-S linkage)
11. Polythionic acid - $H_2(S)_nO_6$ (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: $HClO < HClO_2 < HClO_3 < HClO_4$

Oxidising nature: $HClO > HClO_2 > HClO_3 > HClO_4$

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.

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

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

$$\begin{tikzcd}
\text{Red Phosphorous} \arrow[r, "803K", "high\ P"'] & \alpha\text{-Black Phosphorous} \\
\text{White Phosphorous} \arrow[u, "inert\ medium"'] \arrow[r, "473K", "high\ P"'] & \beta\text{-Black Phosphorous}
\end{tikzcd}$$

ALLOTROPES OF SULPHUR	
Crystalline	**Amorphous**
Rhombic sulphur (α-S) most stable form Monoclinic sulphur (β-S) $\alpha\text{-S} \underset{<95^{o},6^{o}C}{\overset{>95.6^{o}C}{\rightleftharpoons}} \beta\text{-S}$ 95.6°C = transition Temperature both are soluble in CS_2 but insoluble in water	Milk of sulphur Plastic sulphur (γ-S) Colloidal sulphur $\underset{RA}{H_2S} + \underset{OA}{2HNO_3} \xrightarrow{Redox} S + 2NO_2 + 2H_2O$

(a) Density of $\alpha S > \beta S$.

(b) Both are puckered crown shape having S_8 units.

(c) S_2 is paramagnetic sulphur which exist in vapour form at high temperature.

(d) S_6 is chair form of S.

Effect of Temperature

$$S_{8(\alpha)} \xrightarrow{95.5^{o}C} S_{8(\beta)} \xrightarrow{130\text{-}200^{o}C} \text{Viscosity of liquid increase} \xrightarrow{>200^{o}C} \text{Viscosity decrease}$$

SOME IMPORTANT INCREASING ORDER

1. Acidic property

(i) SiO_2, CO_2, N_2O_5, SO_3
(ii) MgO, Al_2O_3, SiO_2, P_4O_{10}
(iii) $HClO$, $HClO_2$, $HClO_3$, $HClO_4$
(iv) CH_4, NH_3, H_2O, HF
(v) SiH_4, PH_3, H_2S, HCl
(vi) H_2O, H_2S, H_2Se, H_2Te
(vii) HF, HCl, HBr, HI
(viii) $InCl_3$, $GaCl_3$, $AlCl_3$
(ix) BF_3, BCl_3, BBr_3, BI_3

2. Bond Angle

(i) CH_4, C_2H_4, C_2H_2
(ii) H_2O, NH_3, CH_4, CO_2
(iii) H_2O, NH_3, CH_4, BH_3
(iv) NO_2^-, NO_2, NO_2^+
(v) H_2Se, H_2S, H_2O
(vi) AsH_3, PH_3, NH_3
(vii) PF_3, PCl_3, PBr_3, PI_3
(viii) NF_3, NCl_3
(ix) NF_3, NH_3, NCl_3
(x) OF_2, OH_2, Cl_2O

3. Basic Character

(i) LiOH, NaOH, KOH, RbOH, CsOH
(ii) $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$
(iii) BeO, MgO, CaO, SrO
(iv) NiO, MgO, SrO, K_2O, Cs_2O
(v) CO_2, B_2O_3, BeO, Li_2O
(vi) SiO_2, Al_2O_3, MgO, Na_2O
(vii) SbH_3, AsH_3, PH_3, NH_3
(viii) F^-, OH^-, NH_2^-, CH_3^-

4. Thermal Stability

(i) Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3
(ii) $BeCO_3$, $MgCO_3$, $CaCO_3$, $BaCO_3$

(iii) $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$
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) $Cr_2O_7^{2-}$, 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

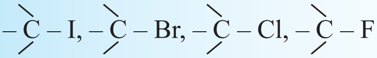
12. Extent of Hydrolysis

(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) 

$-C-I, -C-Br, -C-Cl, -C-F$

(iii) $N-N$, $N=N$, $N\equiv N$

(iv) As – H, Sb – H, P – H, N – 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

CsCl, RbCl, KCl, NaCl

NaI, NaBr, NaCl, NaF

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) $O-O$, $S-S$

(xi) $F-F$, $O-O$, $N-N$, $C-C$, $H-H$

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 (X...H–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

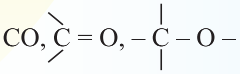
18. Reactivity Towards Air

Be, Mg, Cs, Sr, Ba

19. Bond Length

(i) N_2, O_2, F_2, Cl_2

(ii) $N-N$, $C-N$, $C-C$

(iii) 
CO, $>C=O$, $-\overset{|}{\underset{|}{C}}-O-$

(iv) NO^+, NO, NO^-

(v) O_2, O_3, H_2O_2 (O – 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°48′	H_2O	104°28′
PH_3	93°36′	H_2S	92°
AsH_3	91°48′	H_2Se	91°
SbH_3	91°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	Group 14
B (+3)	C (+4)
Al (+3)	Si (+4)
Ga (+3), (+1)	Ge (+4), (+2)
In (+3), (+1)	Sn (+4), (+2)
Tl (+3), (+1)	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

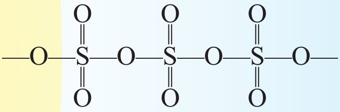
(3) SF_6, PF_5, XeF_6, XeF_4 & XeF_2 exist while SH_6, PH_5, XeH_6, XeH_4, XeH_2 do not exist.

ALLOTROPIC FORM OF SO_3

SO_3 have three allotropic form α-SO_3, β-SO_3 and γ-SO_3.

α-SO_3

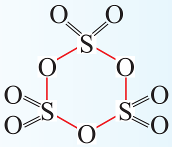
Cross lined solid



$$-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-$$

Polymeric chain structure

β-SO_3



γ-SO_3

(S_3O_9)

cylic trimer

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CHAPTER 27

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

Molten → $Li < Na < K < Rb < Cs$

aqueous → $Li > K \approx Rb > Cs > Na$

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

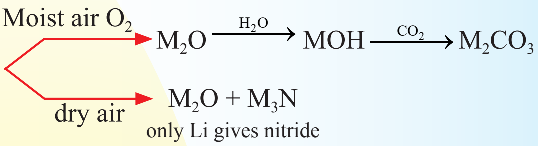
$M_2O \xrightarrow{H_2O} M(OH)$

$M_2O_2 \xrightarrow{H_2O} M(OH) + H_2O_2$

$MO_2 \xrightarrow{H_2O} M(OH) + H_2O_2 + O_2$

With Water : $M + H_2O \rightarrow MOH + H_2$

With Air



With NH_3

$M + (X + Y)\ NH_3 \rightarrow [Na(NH_3)_x]^+ + [e(NH_3)_y]^-$

ammoniated e^-

Paramagnetic, blue colour. In excess of metal dimagnetic and copper bronze colour.

on standing

$Li + NH_3 \rightarrow Li_2NH$ (Lithmide) $+ H_2$

$M(Na/K/Rb/Cs) + NH_3 \rightarrow MNH_2$(amide) $+ H_2$

With Halides

$M + X_2 \rightarrow MX$

K, Rb, Cs forms poly halide due to large size

SIMILARITIES BETWEEN LITHIUM AND MAGNESIUM

(a) Both lithium and magnesium are harder and lighter than other elements in the respective groups.

(b) 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, Li_3N and Mg_3N_2.

(c) The oxides, Li_2O and MgO do not combine with excess oxygen to give a peroxide or a superoxide.

(d) The carbonates of lithium and magnesium decompose easily on heating to form the oxide and CO_2. Solid bicarbonates are not formed by lithium and magnesium.

(e) Both LiCl and $MgCl_2$ are soluble in ethanol.

(f) Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates,

$LiCl.2H_2O$ and $MgCl_2.8H_2O$.

Carbonates

Only Li_2CO_3 decomposes

$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$

Nitrates

$LiNO_3 \xrightarrow{\Delta} Li_2O + NO_2 + O_2$

$MNO_3 \longrightarrow MNO_2 + O_2$ (M = Na/K/Rb/Cs)

$Na_2CO_3.10H_2O$ (Washing Soda)

- In **Solvay's process,** CO_2 gas is passed through saturated brine (NaCl) solution when sparingly soluble $NaHCO_3$ separates out.

  $NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$

  $NH_4HCO_3 + NaCl \rightarrow NaHCO_3\downarrow + NH_4Cl$

  The $NaHCO_3$ formed above is calcined to form Na_2CO_3

  $2NaHCO_3 \xrightarrow{\text{Heat}} Na_2CO_3 + CO_2 + H_2O$

- The reactions taking place at different stages during the manufacture of Na_2CO_3 by Solvay process are given as under :

  (*a*) $2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2\ CO_3$

  $(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3$

  $2NaCl + 2NH_4HCO_3 \rightarrow 2NaHCO_3 + 2NH_4Cl$

  (*b*) Ammonia recovery tower

  $NH_4HCO_3 \xrightarrow{\Delta} NH_3 + CO_2 + H_2O$

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

  (*c*) Calcination of $NaHCO_3$

  $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

(*i*) **Efflorescence :** $Na_2CO_3.10H_2O$ when exposed to air it gives out nine out of ten H_2O molecules.

$$\underset{}{Na_2CO_3.10H_2O} \rightarrow \underset{\text{(Monohydrate)}}{Na_2CO_3.H_2O} + 9H_2O$$

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.

$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{-2}$ and

$$CO_3^{-2} + H_2O \rightleftharpoons \underset{\text{(Carbonic acid)}}{H_2CO_3} + 2OH^-$$

- 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.

$$NaOH \xrightarrow{SiO_2} Na_2SiO_3 + H_2O$$

$$NaOH \xrightarrow{Al_2O_3} 2NaAIO_2 + H_2O$$

(*ii*) **Reaction with non metals :** no reaction with H_2, N_2 and C

$$NaOH \xrightarrow{\Delta/B} Na_3BO_3 + H_2$$

$$NaOH \xrightarrow{\Delta/Si} Na_2SiO_3 + H_2$$

$$NaOH \xrightarrow{\Delta/P_4} NaH_2PO_2 + PH_3$$

$$NaOH \xrightarrow{\Delta/S} Na_2S_2O_3 + Na_2S$$

$$X_2 \xrightarrow{\text{NaOH (cold/dil)}} NaX + NaOX \text{ (Sodium hypo halite)}$$

$$X_2 \xrightarrow{\text{NaOH (Hot/conc.)}} NaX + NaXO_3 \text{ (Sodium Halate)}$$

(*iii*) Reaction with Metal:

$$NaOH \xrightarrow{\text{Alkali metal}} \text{No reaction}$$

$$NaOH \xrightarrow{2Al + 2H_2O} 2NaAlO_2 \text{ (Sodium meta aluminate)} + H_2$$

$$NaOH \xrightarrow{Be} Na_2BeO_2 \text{ (Sodium Berrylate)} + H_2$$

$$NaOH \xrightarrow{Zn} Na_2ZnO_2 \text{ (Sodium zincate)} + H_2$$

$$NaOH \xrightarrow{Sn} Na_2SnO_2 \text{ (Sodium stannite)} + H_2$$

$$NaOH \xrightarrow{Pb} Na_2PbO_2 \text{ (Sodium Plumbite)} + H_2$$

ALKALINE EARTH METALS

Physical properties : General electronic configuration ns^2.

General oxidation state +2.

Atomic/Ionic size Be < Mg < Ca < Sr < Ba

Ionisation energy Be > Mg > Ca > Sr > 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

$Be^{+2} < Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$

CHEMICAL PROPERTIES

With O_2

$$M \xrightarrow{O_2} \underset{\text{(Be, Mg, Ca, Sr, Ba, oxide)}}{MO} \xrightarrow{O_2} \underset{\text{(Ca, Sr, Ba, peroxide)}}{MO_2}$$

With Water

$$M + 2H_2O \rightarrow M(OH)_2 + H_2$$

With Air

In moist air, except Be oxide elements converts into carbonates.

In dry air gives nitride and oxide both

With NH_3

Only Ca, Sr and Ba gives deep blue-black solution of ammoniated electron.

Carbonates

(i) Except $BeCO_3$, all the carbonates are stable towards heat

$$BeCO_3 \xrightarrow{\Delta} BeO + CO_2$$

(ii) Order of decreasing stability

$BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3 > BeCO_3$

Nitrates

(i) Alkaline earth metals forms $M(NO_3)_2$ type nitrates. (M -Alkaline earth metal).

(ii) All alkaline metals nitrates on heating gives oxides and $NO_2 + O_2$

$M(NO_3)_2 \xrightarrow{\Delta} \text{Oxides} + NO_2 + O_2$

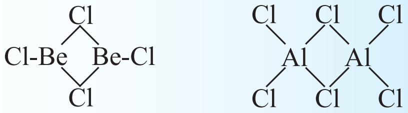
DIAGONAL SIMILARITY BETWEEN BERYLLIUM AND ALUMINIUM

In many of its properties, beryllium resembles Aluminium. Thus

(a) The two elements have same electronegativity and their charge/ radius ratios.

(b) 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 alkalies to form soluble complexes, beryllates $[Be(OH)_4]^{2-}$ and aluminates, $[Al(OH)_4]^-$.

(c) The chlorides of both beryllium and aluminium



have bridged chloride structures in vapour phase.

(d) Salts of these metals form hydrated ions, Ex. $[Be(OH_2)_4]^{2+}$ and $[Al(OH_2)_6]^{3+}$ in aqueous solution. Due to similar charges/radius rations of beryllium and aluminium ions have strong tendency to form complexes. For example beryllium forms tetrahedral complexes such as BeF_4^{2-} and $[Be(C_2O_4)_2]^{2-}$ and aluminium forms octahedral complexes like AlF_6^{3-} and $[Al(C_2 O_4)_3]^{3-}$.

- Be_2C on treatment with H_2O forms CH_4 while CaC_2 forms C_2H_2.

$$Be_2C + 2H_2O \rightarrow 2\ BeO + \underset{\text{Methane}}{CH_4}$$

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

CHLORIDE OF ALKALINE EARTH METAL

- $BeCl_2$ in the vapour phase above 900ºC is monomeric; below 900ºC 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 exits as a monomer.
- Anhydrous $MgCl_2$ cannot be prepared by the simple heating of hydrated magnesium chloride $MgCl_2, 6H_2O$, as it gets hydrolysed to magnesium oxide.

$$MgCl_2.6H_2O \xrightarrow{\text{Heat}} MgO + 2HCl + 2H_2O$$

- 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

(i) Charcoal cavity test. On heating on a charcoal cavity with one drop of $Co(NO_3)_2$, a pink colour is imparted to the residue CoO.MgO.

(ii) The salt solution when mixed with NH_4Cl and NH_4OH and finally treated with soluble phosphates forms a with precipitate of magnesium ammonium phosphate.

$$MgSO_4 + Na_2HPO_4 + NH_4OH \rightarrow \underset{\text{white ppt.}}{Mg(NH_4)PO_4} + Na_2SO_4 + H_2O$$

CALCIUM CYANAMIDE

- Calcium cyanamide ($CaCN_2$) is prepared by heating a mixute of CaC_2 in an atmosphere of N_2 at 1270-1370K with CaF_2.

  $$CaC_2 + N_2 \xrightarrow[1270-1370K]{CaF_2} CaCN_2 + C$$

  It trade name is Nitrolim.
- Calcium cyanamide ($CaCN_2$) is a slow acting manure and is preferred to soluble compounds like $NaNO_3$ or $(NH_4)_2$ 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.
- $CaCN_2 + H_2O + CO_2 \rightarrow CaCO_3 + H_2NCN$
- $H_2NCN + H_2O \rightarrow \underset{\text{Urea}}{H_2NCONH_2}$
- $H_2NCONH_2 + H_2O \rightarrow CO_2 + 2NH_3$

OXIDE OF CALCIUM

Quick lime (CaO) is obtained when limestone is heated at about 1000ºC. 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 $Ca(OH)_2$.

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 ($CaSO_4.2H_2O$) found in nature, when heated, it first changes from monoclinic form to orthorhombic form without loss of water. At 120ºC, it loses three-fourth of its water of crystallisation and forms hemihydrate ($CaSO_4$. 1/2 H_2O) known as plaster of Paris.
- Plaster of Paris has the property of setting to a hard mass $CaSO_4$. $2H_2O$, 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 200ºC, it forms anhydrous calcium sulphate which is known as dead plaster. It hs no setting property.

Cement

Cement is an important building material. The average composition of portland cement is : CaO 61.5%, SiO_2 22.5%, Al_2O_3 7.5%. Cement consists of :

Tricalcium silicate $3CaO.SiO_2$

Dicalcium silicate $2CaO.SiO_2$

Tricalcium aluminate $3CaO.Al_2O_3$

Tetracalcium alumino - ferrite $4CaO. Al_2O_3. Fe_2O_3$

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, $Ca_9(PO_4)_6. Ca(OH)_2$ 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, $Ca_9(PO_4)_6.CaF_2$.

HYDROLITH

Hydrolith (CaH_2) is calcium hydride & on hydrolysis for calcium hydroxied & librate hydrogen.

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CHAPTER 28

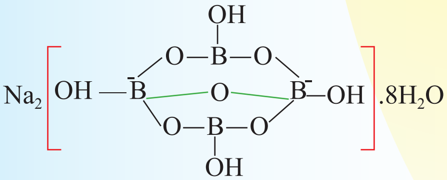
p-Block

13th-GROUP

- Some important ores of Boron are given as under.
    - (i) Boric acid, H_3BO_3
    - (ii) Borax, $Na_2B_4O_7.10H_2O$
    - (iii) Colemanite, $Ca_2B_6O_{11}.5H_2O$
- Some important minerals of aluminium are given as under.
    - (i) Corundum, Al_2O_3
    - (ii) Bauxite, $Al_2O_3.2H_2O$
    - (iii) Cryolite, Na_3AlF_6
    - (iv) Feldspar, $KAlSi_3O_8$

BORAX $Na_2[B_4O_5(OH)_4].8H_2O$

$Na_2[B_4O_5(OH)_4].8H_2O$



Properties

(i) It is a white crystalline solid of formula $Na_2B_4O_7.10H_2O$. In fact it contain the tetranuclear units $[B_4O_5(OH)_4]^{2-}$ and correct formula; therefore, is $Na_2[B_4O_5(OH)_4].8H_2O$.

(ii) Hydrolysis

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$$

(iii) Heating

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} \underset{\text{Swells up}}{Na_2B_4O_7} \xrightarrow{\Delta} \underset{\substack{\text{Sodium}\\\text{metaborate}}}{2NaBO_2} + \underset{\substack{\text{Boric}\\\text{anhydride}}}{B_2O_3}$$

(iv) When borax is heated in a Bunen burner flame with CoO on a loop of platinum wire, a blue coloured $CO(BO_2)_2$ bead is formed.

DIBORANE, B_2H_6

Preparation

(i) $\underset{\text{or }LiBH_4}{3LiAlH_4} + 4BF_3 \longrightarrow 3LiF + \underset{\text{or }3(BF_3)}{3AlF_3} + 2B_2H_6$

(ii) **Laboratory method**

$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$

(iii) **Industrial scale**

$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$

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 :

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$; $\Delta_cH^{\circ} = -1976$ kJ mol^{-1}

(iv) Hydrolysis :

$B_2H_6(g) + 6H_2O(\ell)$ (Cold is enough) $\rightarrow 2B(OH)_3(aq) + 6H_2(g)$

$B_2H_6 + HCl \text{ (dry)} \xrightarrow[AlCl_3]{\text{anh.}} B_2H_5Cl + H_2$

(v) Reaction with Lewis Bases

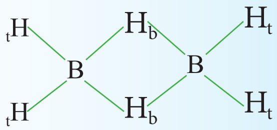
(a) $B_2H_3 + 2NMe_3 \rightarrow 2BH_3.NMe_3$

(b) $B_2H_6 + 2CO \rightarrow 2BH_3.CO$

(c) $3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\text{Heat}} 2B_3N_3H_6 + 12H_2$

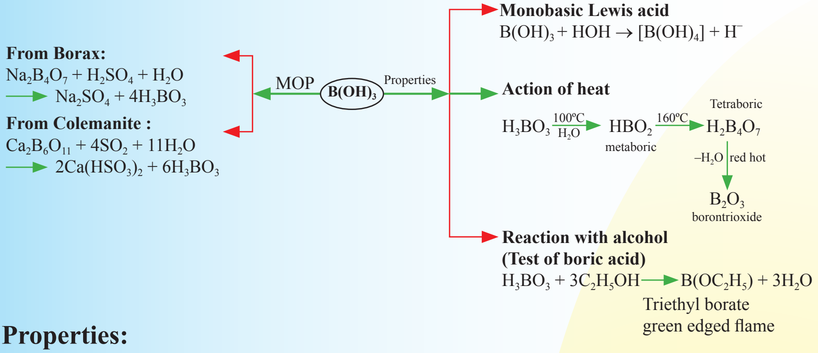
(vi) Reaction with ROH :

$B_2H_6 + 6ROH \rightarrow 2B(OR)_3 + 6H_2O$



dimer due to formation of 3 centre-2e-bond inorganic benzene.

ORTHOBORIC ACID [H_3BO_3 OR $B(OH)_3$]



From Borax:

$Na_2B_4O_7 + H_2SO_4 + H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$

From Colemanite :

$Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$

MOP

$B(OH)_3$

Properties

Monobasic Lewis acid

$B(OH)_3 + HOH \rightarrow [B(OH)_4] + H^-$

Action of heat

$H_3BO_3 \xrightarrow[H_2O]{100^\circ C} \underset{\text{metaboric}}{HBO_2} \xrightarrow{160^\circ C} \overset{\text{Tetraboric}}{H_2B_4O_7} \xrightarrow[\text{red hot}]{-H_2O} \underset{\text{borontrioxide}}{B_2O_3}$

Reaction with alcohol

(Test of boric acid)

$H_3BO_3 + 3C_2H_5OH \longrightarrow B(OC_2H_5) + 3H_2O$

Triethyl borate

green edged flame

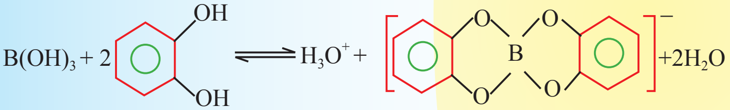
Properties:

- Boric acid is a weak monobasic acid

  $$B(OH)_3 + 2H_2O \Leftrightarrow H_3O^{\oplus} + [B(OH)_4]^-$$

  $$pKa = 9.25$$

- 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 polhydroxy 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 it's 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, $Al_2O_3.2H_2O$. First, bauxite is purified from the impurities (Red bauxite contains Fe_2O_3) 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 Fe_2O_3 and then digested at 423K with conc. NaOH solution for a few hours when Al_2O_3 gets dissolved to give a solutions of $[Al(OH)_4]^{-1}$ The basic oxide impurities such as Fe_2O_3 are not affected.

  $$Al_3O_3 + 2OH^{-1} + 3H_2O + \underset{\text{Aluminate ion}}{2[Al(OH)_4]^{-1}}$$

Fe_2O_3 left undissolved iss filtered off. The treatment of $[Al(OH)_4]^{-1}$. solution with a weak acid precipitate pure $Al(OH)_3$.

$$[Al(OH)_4]^{-1} + H^+ \rightarrow \underset{\text{(White ppt.)}}{Al(OH)_3} + H_2O$$

The $Al(OH)_3$ precipitate is removed by filtration and ignited to get alumina, Al_2O_3.

- **Hall's process** involves the fusion of the ore with Na_2CO_3 when soluble sodium meta aluminate, $NaAlO_2$ is produced. This is extracted with water when Fe_2O_3 is left as a residue.

$$Al_2O_3 + Na_2CO_3 \rightarrow \underset{\text{Sodium meta aluminate}}{2NaAlO_2} + CO_2$$

The water extract is heated upto 333K and CO_2 is passed through it. $Al(OH)_3$ is precipitated due to hydrolysis and is ignited to get alumina, Al_2O_3.

$$2NaAlO_2 + 3H_2O + CO_2 \rightarrow 2Al(OH)_3 + Na_2CO_3$$

- **Serpeck's process** involves the heating of bauxite with coke in a current of N_2 at 2075K. The SiO_2 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.

$$SiO_2 + 2C \rightarrow Si\uparrow + 2CO\uparrow$$

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$$

$$\underset{\text{Aluminium nitride}}{AlN} + 3H_2O \rightarrow Al(OH)_3 + NH_3$$

Electrolysis of Al_2O_3 to form aluminium. Pure alumina is dissolved in fused cryolite, Na_3AlF_6 at 1225 K by current of 100 amp eres and 6-7 volts to get Al. The Al obtained is purified by Hoope's process.

ALUMINIUM TRIFLUORIDE

- **Aluminium trifluride** (AlF_3) is different from other trihalides of Al in being insoluble and nonvolatile in nature. In AlF_3 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 ($AlCl_3$) in the pure and anhydrous state is a white solid but commercial samples are yellowish due to the impurity of $FeCl_3$.
- Anhydrous $AlCl_3$, in the crystalline state possesses a closely pakced 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 $[Al(H_2O)_6]Cl_3$ with enthalpy of solution –300 KJ mol^{-1}. Due to this strong Al – O linkage hydrate connot be dehydrated on heating to form $AlCl_3$.

  $2[Al(H_2O)_6]\ Cl_3 \xrightarrow{\Delta} Al_2O_3 + 6HCl + 9H_2O$

- Aluminium chloride, is a polymeric solid which exists as a dimer Al_2Cl_6 between 200–400ºC and then monomer up to 800ºC.
- **Thermite welding,** Aluminium has got a very high affinity for oxygen.

  $$4Al + 3O_2 \rightarrow 2Al_2O_3$$
  $$\Delta H = -3230\ KJ\ mol^{-1}$$

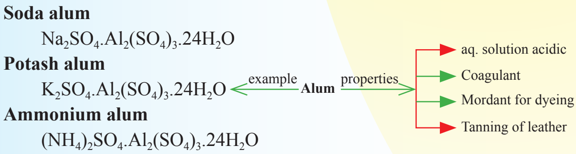
  It, therefore, displaces metals less electropositive than itself from oxides. The large amount of heat produced is used in welding rails or heavy machinery without removing them from their position. This is called thermite welding or Gold Schmidt's aluminothermic process. In this process, a mixture of 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 C_2H_5OH and BO_3^{3-} salt with conc. H_2SO_4 burns with green edge flame due to the formation of ethyl borate.

  $H_3BO_3 + 3C_2H_5OH \rightarrow \underset{\text{Ethyl borate}}{B(OC_2H_5)_3} + 3H_2O$

- **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 $[M_2SO_4.M_2'(SO_4)_3.24H_2O]$

Alums are the double salt of Type $[M_2SO_4.M_2'(SO_4)_3.24H_2O]$
M : Monovalent Cation: Na^+, K^+, Rb^+, Cs^+, NH_4^+
M′ : Trivalent Cation: Al^{3+}, Fe^{3+} & Cr^{3+}



Soda alum
$Na_2SO_4.Al_2(SO_4)_3.24H_2O$
Potash alum
$K_2SO_4.Al_2(SO_4)_3.24H_2O$
Ammonium alum
$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$

Pseudo alums are double sulphates of a divalent and a trivalent metals which crystallize with twenty four water molecules of crystallization, for example.

(i) $MnSO_4.\ Al_2(SO_4)_2.24H_2O$ (ii) $FeSO_4.Al_2(SO_4)_2.24H_2O$

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 $C >> Si > Ge \approx Sn$. 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

$\Rightarrow$ $C^{+4} \rightarrow Pb^{+4}$ (Stability)

$\Rightarrow$ $C^{+2} \rightarrow Pb^{+2}$ (Stability)

$\Rightarrow$ Pb^{+4} compounds are strong oxidizing agent.

$\Rightarrow$ PbI_4 does not exist.

- Trimethylamine $(CH_3)_3N$ is pyramidal while Trisilylamine $N(SiH_3)_3$ 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 : $(R_2SiO)_n$. Where $R = -CH_3, -C_2H_5, -C_6H_5$

$$(i)\quad R_2SiCl_2 + 2H_2O \xrightarrow{-2HCl} R_2Si(OH)_2 \xrightarrow[-H_2O]{\Delta}$$

Linear Silicones/Cyclic Silicones

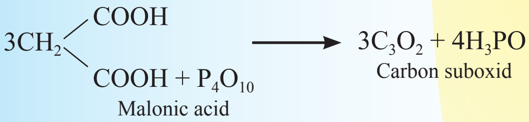
$$(ii)\quad R_3SiCl + H_2O \xrightarrow{HCl} R_3Si(OH)_2 \xrightarrow[-H_2O]{\Delta} \text{Dimer Silicones}$$

$$(iii)\quad RSiCl_3 + 3H_2O \xrightarrow{-3HCl} RSi(OH)_3 \xrightarrow[-H_2O]{\Delta}$$

Crossed Linked Silicones

CARBON SUBOXIDE

- Carbon suboxide (C_3O_2) is an foul smellting gas which can be prepared by the dehydration of malonic acid with P_4O_{10}.



$$3CH_2\begin{matrix} \diagup COOH \\ \diagdown COOH \end{matrix} + P_4O_{10} \longrightarrow \underset{\text{Carbon suboxid}}{3C_3O_2} + 4H_3PO$$

Malonic acid

On heating upto 200°C, it decomposes into CO_2 and carbon.

$$C_3O_2 \xrightarrow{200°C} CO_2 + 2C$$

The molecule is throught to have a linear structure.

$$O = C = C = C = O$$

OXIDE OF LEAD

- **Read lead (Pb_3O_4)** is considered to be mixture of lead monoxide and lead dioxide and it is written as $(PbO_2 \cdot 2PbO)$.
- **Lead dioxide (PbO_2).** It is a brown powder obtained by the treatment of red lead with HNO_3.

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O$$

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_2SO_4	HNO_3
PbO	Na_2PbO_2	$PbCl_2$	$PbSO_4$	$Pb(NO_3)_2$
PbO_2	Na_2PbO_3	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2$
Pb_2O_3	$Na_2PbO_2 + NaPbO_3$	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2 + PbO_2$
Pb_3O_4	$Na_2PbO_2 + Na_2PbO_3$	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2 + PbO_2$

Tin and Its Compound

- **Action of conc. HNO_3 on tin**

  (*a*) Dilute HNO_3

  $$4Sn + 10HNO_3 \rightarrow 4\,Sn(NO_3)_2 + HN_4NO_3 + 3H_2O$$

  (*b*) Hot conc. HNO_3

  $$Sn + 4HNO_3 \rightarrow \underset{\text{Metastannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$$

  Action of conc. NaOH on tin

  $$\Rightarrow \quad Sn + 2NaOH + H_2O \rightarrow Na_2SnO_3 + 2H_2\uparrow$$

$SnCl_2$

- $SnCl_2 \cdot 2H_2O$ on heating undergoes to form it's 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 ($HgCl_2$) to a white precipitate of mercurous chloride (Hg_2Cl_2)

  $$2Hg^{2+} + 3Cl^{-} + Sn^{2+} \rightarrow \underset{\text{Mercurous chloride}}{Hg_2Cl_2} + Sn^{+4}$$

  which finally turns to metallic mercury (dark grey or black)

  $$Hg_2Cl_2 + SnCl_2 \rightarrow \underset{\text{Black}}{2Hg_2}\downarrow + SnCl_4$$

- **Mosaic gold (SnS_2):** 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 NH_4Cl in a retort.

  $$Sn + 4NH_4Cl \rightarrow (NH_4)_2SnCl_4 + H_2 + 2NH_3$$

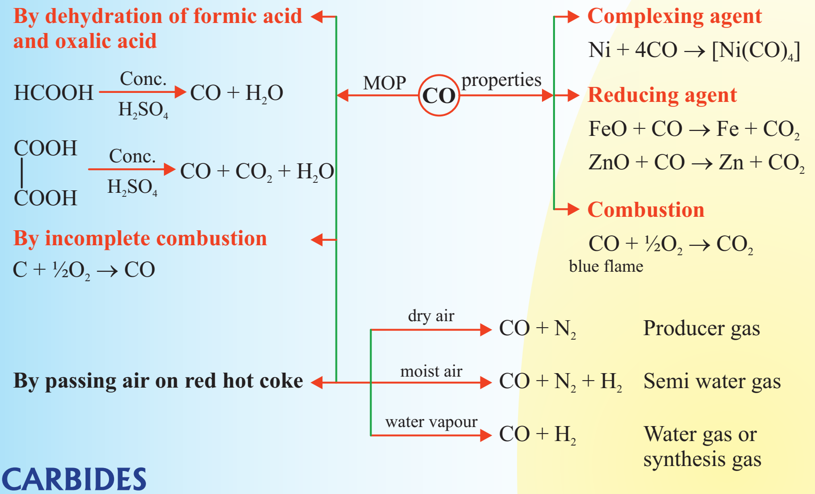
  $$2(NH_4)_2SnCl_4 + 2S \rightarrow SnS_2 + (NH_4)_2SnCl_6 + 2NH_4Cl$$

- **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, poisionous gas

$\boxed{C \overset{\leftarrow}{\equiv} O}$



By dehydration of formic acid and oxalic acid

$HCOOH \xrightarrow[H_2SO_4]{Conc.} CO + H_2O$

$\begin{array}{l} COOH \\ | \\ COOH \end{array} \xrightarrow[H_2SO_4]{Conc.} CO + CO_2 + H_2O$

By incomplete combustion

$C + ½O_2 \rightarrow CO$

By passing air on red hot coke

$\xrightarrow{\text{dry air}} CO + N_2$ Producer gas

$\xrightarrow{\text{moist air}} CO + N_2 + H_2$ Semi water gas

$\xrightarrow{\text{water vapour}} CO + H_2$ Water gas or synthesis gas

Complexing agent

$Ni + 4CO \rightarrow [Ni(CO)_4]$

Reducing agent

$FeO + CO \rightarrow Fe + CO_2$

$ZnO + CO \rightarrow Zn + CO_2$

Combustion

$CO + ½O_2 \rightarrow CO_2$

blue flame

CARBIDES

Binary compounds of carbon with other elements (except hydrogen) are known as carbides

CARBIDES

Ionic Carbide	Covalent Carbide	Interestial Carbides
C+ higher electropositive element (IA, IIA & Al)	C + Non-metals (like B & Si)	C + transition metals
Eg. Be_2C, Mg_2C_3, Al_4C_3, CaC_2	Eg. B_4C, SiC	Eg. TiC,WC

15th–GROUP ELEMENTS

Nitrogen Family

1. Nitrogen and phosphorus are **non-metals**, arsenic and antinomy **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 characterissed 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,

   (i) $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

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 antinomy 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 in BiF_5.

⇒ All the oxidation states from +1 to +4 tend to disproportionate in acidic solution :

exp: $3HNO_2 \rightarrow HNO_3 + 2NO$

⇒ All the intermediate oxidation states disproportionate into +5 and –3

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$

$$H_3PO_2 \xrightarrow{\Delta} H_3PO_4 + PH_3$$

⇒ Hybride of 15th group elements:

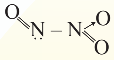
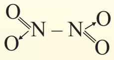
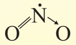
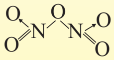
$NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$	Basic character
$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$	Stability
$PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$	Boiling Point
$PH_3 < AsH_3 < SbH_3 < NH_3$	Melting Point
$NH_3 > PH_3 > AsH_3 > SbH_3$	Bond Energy

⇒ Penta oxide of 15th group element is acidic. N_2O_3, P_2O_3 are acidic, As_2O_3, Sb_2O_3 are amphoteric with Bi_2O_3 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	$N \equiv N \rightarrow O$
NO Nitric oxide	2	Colourless gas	$N = O$

Oxide of Nitrogen	Oxide State	Physical Appearance	Structure
N_2O_3 Dinitrogen trioxide	+3	Blue colour solid	
N_2O_4 Dinitrogen tetraoxide	+4	Colourless solid	
NO_2 Nitrogen dioxide	+4	Brown gas	
N_2O_5 Dinitrogen pentaoxide	+5	Colourless solid	

Oxides of Nitrogen

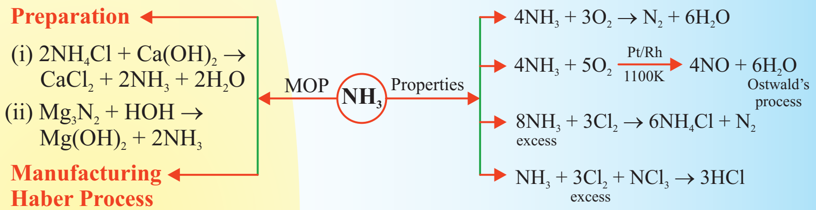
Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen oxide]	N_2O	+1	$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+3	$2NO + N_2O_4 \xrightarrow{250\text{ K}} 2N_2O_3$	Blue solid, acid blue liquid (–30°C)
Nitrogen dioxide [Nitrogen (IV) oxide]	NO_2	+4	$2Pb(NO_3)_2 \xrightarrow{673\text{ K}} 4NO_2 + 2PbO + O_2$	Brown gas, acidic
Dinitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+4	$2NO_2 \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$	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_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	Colourless solid, acidic

COMPOUNDS OF NITROGEN FAMILY

Ammonia (NH_3)

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



Preparation

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

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

Manufacturing
Haber Process

MOP — NH_3 — Properties

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

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

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

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

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

Nitric Acid (NHO_3)

Preparation

Ostwald's process

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

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

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

Properties

HNO_3, nitric acid was earlier called as aqua fortis (meaning strong water). It usually acquires yellow colour. Due to its decomposition by sunlight into NO_2. It acts as a strong oxidising agent.

Reaction with $FeSO_4$

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

Reaction with non-metals

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

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

Reaction with metals

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

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

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

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

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

Phosphine (PH_3)

Preparation

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

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

Laboratory preparation

$$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$$

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

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

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

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

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 phosporic 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).

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

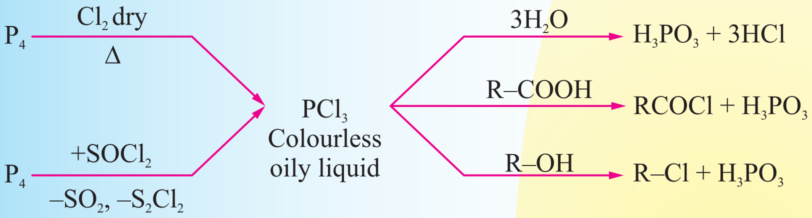
$$2H_3PO_2 \xrightarrow{\text{Heat}} H_3PO_4 + PH_3$$

- **Holme's signals:** A mixture of Ca_3P_2 and CaC_2 on treatment with H_2O forms PH_3 and P_2H_4 along with C_2H_2. The mixture burns with a bright

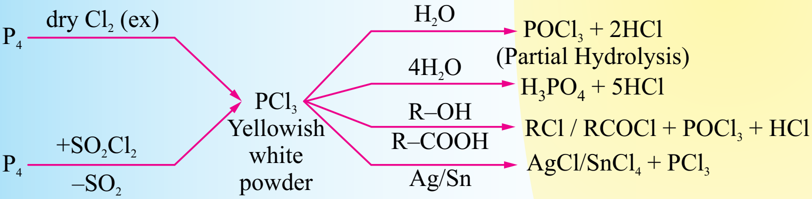
$$Ca_3P_2 + 6H_2O + 3Ca(OH)_2 + 2PH_3$$
$$CaC_2 + H_2P \rightarrow Ca(OH)_2 + C_2H_2$$

- Smoke screens, involve the use of calcium phosphide, Ca_3P_2. The PH_3 gas obtained from Ca_3P_2 catches fire to give the needed smoke.
- **Phosphatic slag or Thomas slag or Basic slag** is obtained as a biproduct 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 : $2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$

- 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 does not form dihalides.

  e.g. OF_2, Cl_2O_6, I_2O_5, etc.

SODIUM THIOSULPHATE $Na_2S_2O_3 \cdot 5H_2O$

- **Preparation**

  (a) $Na_2SO_3 + S \xrightarrow{\text{Boil}} Na_2S_2O_3$

  (b) $4S + 6NaOH \xrightarrow{\text{Boil}} Na_2S_2O_3 + 2Na_2S + 3H_2O$

  (c) $2Na_2S + 3SO_2 \xrightarrow{\text{Boil}} 2Na_2S_2O_3 + S$

  (d) Spring's reaction

  $Na_2S + Na_2SO_3 + I_2 \xrightarrow{\text{Heat}} Na_2S_2O_3 + 2NaI$

- **Concentrated $Na_2S_2O_3$** does not give a white ppt. with $AgNO_3$. This is because silver thiosulphate formed is readily soluble in excess of sodium thiosulphate forming soluble complex.

$$3S_2O_3^{2-} + Ag_2S_2O_3 \rightarrow 2\underset{\text{soluble}}{[Ag(S_2O_3)_2]^{3-}}$$

Reaction with oxidizing agent

(i) $Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl + S$

(ii) $2Na_2S_2O_3 + I_2 \rightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + 2NaI$

This reaction forms the basis of iodometric estimation of $Cr_2O_7^{2-}$ and Cu^{2+} salts.

(iii) $3S_2O_3^{2-} + 2Fe^{3+} \Leftrightarrow \underset{\text{Violet}}{[Fe(S_2O_3)_2]^{-1}}$

The violet colour disappear quickly due to the reduction of ferric chloride by $S_2O_3^{2-}$ ions,

$2Fe^{3+} + 2S_2O_3^{2-} \rightarrow 2Fe^{+2} + S_4O_6^{2-}$

(iv) $2CuCl_2 + 2Na_2S_2O_3 \rightarrow 2CuCl + Na_2S_4O_6 + 2NaCl$

(v) $AuCl_3 + 2S_2O_3^{2-} \rightarrow AuCl + S_4O_6^{2-} + 2Cl^-$

$AuCl + 2S_2O_3^{2-} \rightarrow [Au\,(S_2O_3)_2]^{3-} + Cl^-$

- **Sulphur trioxides** (SO_3) is a white crystalline solid with melting point 290 K and boiling point 318 K.
- SO_3 is prepared by the direct oxidation of SO_2 with atmospheric oxygen in presence of finally divided Pt or V_2O_5 at a pressure of 2 bar and temperature 720 K.

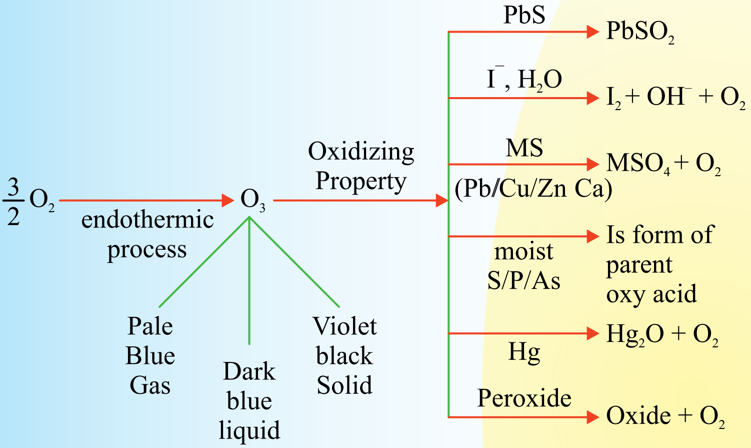
- SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.

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

SO$_3$ reacts with water to produce H_2SO_4 and large amount of heat is evolved.

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

OZONE



* Fishy odour, Highly toxic.

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

HYDROGEN PEROXIDE

Preparation

(i) $Na_2O_2 + H_2O$ (icecold) $\rightarrow NaOH + H_2O_2$

(ii) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

(Now a day conc. H_3PO_4 is used)

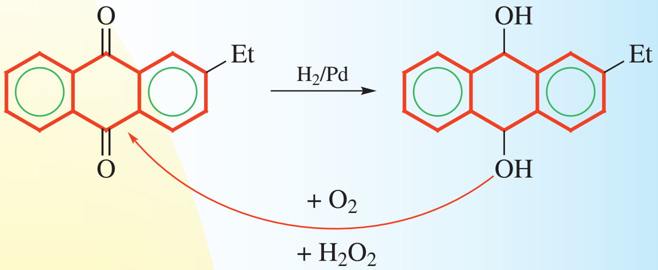
(iii) $2H_2SO_4 \rightarrow 2H^+ + 2HSO_4^-$

Anode : $2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$

Cathode : $2H^+ + e^- \rightarrow H_2$

$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$

(iv)



Properties

Oxidizing Property

(i) $H_2O_2 \xrightarrow{PbS} PbSO_4$

(ii) $H_2O_2 \xrightarrow{BaSO_3} BaSO_4 + H_2O$

(iii) $H_2O_2 \xrightarrow{H_2S/HI} S/I_2 + H_2O$

(iv) $H_2O_2 \xrightarrow{F^{+2}/H^-} Fe^{+3} + H_2O$

(iv) $H_2O_2 \xrightarrow{Cr^{+3}/OH^-} Cr^{+6} + H_2O$

Reducing Property

(i) $H_2O_2 \xrightarrow{Fe^{+3}/OH^-} Fe^{+2} + O_2$

(ii) $H_2O_2 \xrightarrow{Pb^+\ Grids} PbO$

(iii) $H_2O_2 \xrightarrow{Cl_2/Br_2} PbO$

(iv) $H_2O_2 \xrightarrow{MnO_4^-/OH^-} HX \downarrow + O_2$

(v) $H_2O_2 \xrightarrow{MnO_4^-/H^+} Mn^{+2} + O_2$

(vi) $H_2O_2 \xrightarrow{Cr_2O_7^{2-}/H^+} Cr^{+2} + O_2$

- Tailing of mercury is due to the formation of mercury oxide when Hg reacts with ozone.

  $$2Hg + O_3 \rightarrow Hg_2O + O_2$$

  As a result of it, mercury looses it's 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 resture 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.

$$\underset{\text{Black}}{PbS} + 4H_2O_2 \rightarrow \underset{\text{White}}{PbSO_4} + 4H_2O$$

- Antichlor action H_2O_2 is due to its tendency to reduce the excess of chlorine from bleaching powder to HCl.

⇒ $NH_2 \cdot NH_2 + H_2O_2$ as rocket propellant.

⇒ 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.

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

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

(b) Production of catalyst : Oxides of nitrogen.

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

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

(c) Reaction in lead chamber

$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

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

Contact process

The steps involved are:

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

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

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + x \text{ cal}$$

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

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

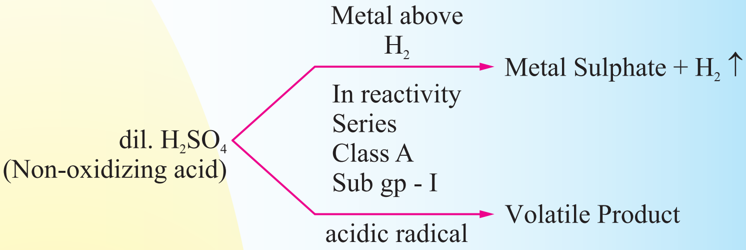
$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$$

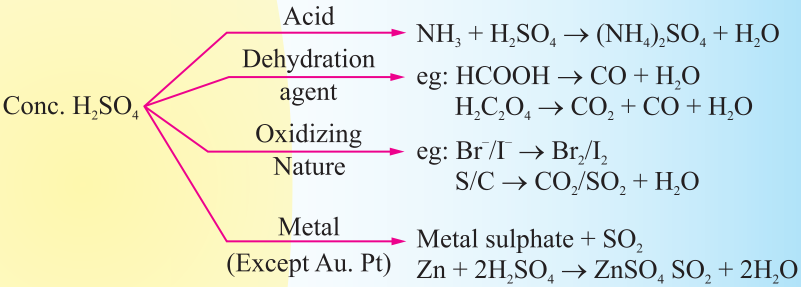
$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

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

It is strong dibasic acid.

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





Uses :

In lead storage batteries.

In manufacture of paints and pigments.

In metallurgy for electrolytic refining of metals.

17th–GROUP ELEMENTS

1. The electron affinity values (in KJ mol^{-1}) for 17 group element are given below:

F	Cl	Br	I
333	349	325	296

2. 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.
3. They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is $F_2 > Cl_2 > Br_2 > I_2$.

4. In general, a halogen oxidises halide ions of higher atomic number.

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

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

$Br_2 + 2I^- \rightarrow 2Br^- + I_2$

5. Reaction with water :

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

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

(where X = Cl or Br)

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

6. Halogens form many oxides with oxygen but most of them are unstable.

7. Flourine 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 the oxygen. Both are strong fluorinating agents.

8. O_2F_2 oxidises plutonium to PuF_6 and the reaction is issued 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, I > Cl > 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 ↑.

$$HF < HCl < HBr < HI$$

- Bond strength is inversely, proportional to bond length i.e., larger the bond length, lower the bond strength is

$$HF > HCl > HBr > HI$$

- Higher the bond dissociation energy greater will be thermal stability. Thus, thermal stability follows the order.

$$HF > HCl > HBr > HI$$

REDUCING CHARACTER

The reducing character of hydrogen halides increases down the group as

$$HF < HCl < HBr < HI$$

$$2HX \rightarrow H_2 + X_2$$

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.

$$HF < HCl < HBr < HI$$

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.

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{\text{Sunlight}} 2HCl_{(g)}$$

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

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

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

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

Metal + Hydrochloric → Metal chloride + Hydrogen

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

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

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

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

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

Reducing property : HCl is a strong reducing agent.

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

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 (N_3^-), Aziothnio carbonate ($SCSN_3^-$) and isocyanate (ONC^-).

CHLORINE (Cl_2)

Preparation : By oxidation of conc. HCl.

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

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

Manufacture :

Weldon's process **:** By heating pyrolusite with conc. HCl.

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

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

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

Bleaching action and oxidising property

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

$HOCl \rightarrow HCl + [O]$

Coloured matter + nascent : [O] → Colourless matter

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

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

Action of hydrogen **:**

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

Displacement reactions :

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

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

Action of NaOH :

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

$$\underset{\text{(hot and conc.)}}{6NaOH} + \underset{\text{dry}}{3Cl_2^0} \rightarrow 5NaCl^{-1} + \underset{\text{sodium chlorate}}{NaCl^{+5}O_3} + 3H_2O$$

Addition reactions :

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2$$

$$CO + Cl_2 \rightarrow COCl_2$$

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

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.

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

$$SiF_4 + H_2F_2 \rightarrow H_2SiF_6$$

This is called etching of glass.

- Iodine is slightly soluble in water but much more soluble in KI due to the formation of KI=3.

$$KI + I_2 \rightarrow KI_3$$

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

OXY-ACID

- The acidic strength of the oxoacids of halogen decreases in the following order.

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

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

$$HClO > HBrO > HIO$$

18th–GROUP ELEMENTS

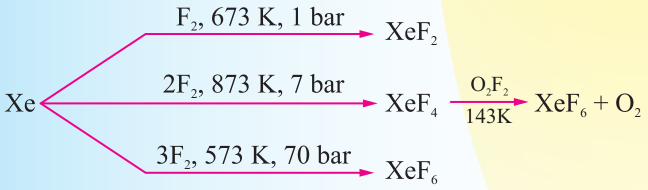
1. Relative Abundance :

   $Ar > Ne > Kr > He > Xe > Rn$
2. Melting and Boiling point :

   $Rn > Xe > Kr > Ar > Ne > He$
3. He has the lowest boiling point among all element.
4. Noble gases are monoatomic, colourless, odourless, spraingly soluble in water and diffusing through most commonly used laboratry materials.
5. $O_2[PtF_6]$ is the first noble gas compound.
6. Ar, Kr and Xe from clathrate compound when pass in ice with high pressure.

   $A\cdot 6H_2O$ (A = Ar/Kr/Xe)

Preparation of Xe-Fluoride



Properties

Fluoride donor : Eg. $XeF_2 + \underset{(M=As/Sb/P)}{MF_5} \longrightarrow [XeF_4]^+ [MF_6]^-$

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

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

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

Hydrolysis

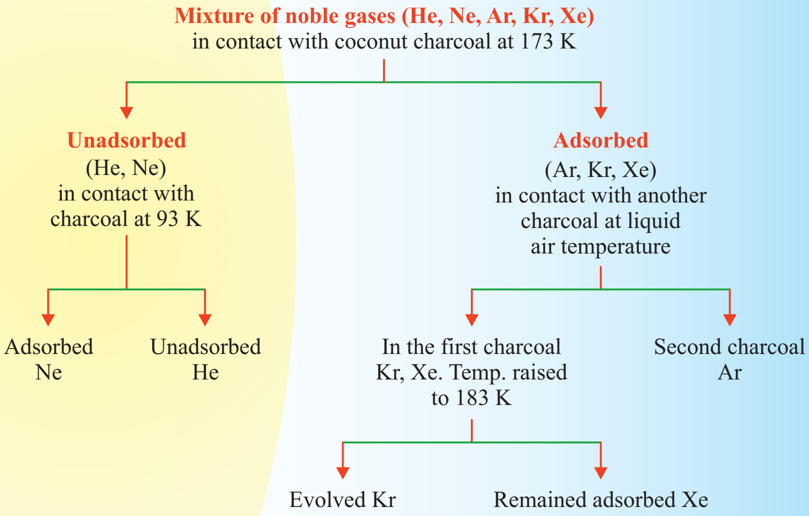
$$XeF_2 \xrightarrow{H_2O} Xe + 2HF + \frac{1}{2}O_2$$

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

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

NOBLE GAS

In Dewar's method, the separation of noble gases is summerized below:



The viscosity of He is extremely low, about 1/100th of hydrogen gas.

CHAPTER 29

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

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

$$\text{Exceptions}\left\{\begin{array}{l} Cr = 4s^1 3d^5 \\ Cu = 4s^1 3d^{10},\ Pd = 5s^0 4d^{10} \end{array}\right.$$

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 $Sc > Ti > V > Cr > Mn \geq Fe \simeq Co \simeq Ni \leq Cu < Zn$

In a group 3d to 4d series increases but 4d and 5d series nearly same due to poor shielding of f electron. (Lanthanide contraction)

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

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

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

In a series on increasing number of unpaired e^- melting point increases upto Cr then decreases.

$$\text{Sc} < \text{Ti} < \text{V} < \underset{\substack{\downarrow \\ \text{Half filled } d^5 \\ \therefore \text{ weak metallic bond}}}{\text{Cr}} > \text{Mn} < \text{Fe} > \text{Co} > \text{Ni} > \text{Cu} > \underset{\substack{\downarrow \\ \text{Fully filled } d^{10} \\ \therefore \text{ weak metallic bond}}}{\text{Zn}}$$

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

E.N. Exception $\text{Zn} < \text{Cd} < \text{Hg}$

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

3d series

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

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

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

Electrical conductor

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

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 MnF_4 while oxide is Mn_2O_7

⇒ Mn show maximum number of oxidation state (+2 to +7) among 3d series.

⇒ Beyond Mn, trihalide are not observe except FeX_3 (X = Cl/Br/I) & CoF_3

⇒

V_2O_3	V_2O_4	V_2O_5
basic	basic	amphoteric

⇒

CrO	Cr_2O_3	CrO_3
basic	amphoteric	acidic

⇒

MnO	MnO_2	Mn_2O_7
basic	amphoteric	acidic

⇒ CuI_2 does not exist

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

⇒ In aqueous, Cu^{+} disproportinated 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 Mo(+6) & W(+6) are more stable than 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 definate 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 from 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, Mn_4N, Fe_3H 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 = V_2O_5

Haber process = $Fe_2O_3 + Al_2O_3 + K_2O$

Fenton's reagent = $FeSO_4 + H_2O_2$

Decomposition of $KClO_3$ = MnO_2

Ostwald process = Pt/Rh

Zeigler Natta = $TiCl_4 + (C_2H_5)_3\,Al$

Hydrogenation of Alkene = Ni/Pd

Wilkinson's catalyst = RhCl + PPh_3

Important reactions of d-block elements

(a) $Cu^{2+} + 4I^{-} \longrightarrow Cu_2I_{2(s)} + I_2$

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

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

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

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

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

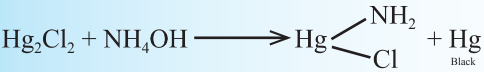
(d) $AgNO_3(s) \xrightarrow{\text{Heating}} Ag + NO_2 + \frac{1}{2}O_2$

$AgCO_3(s) \xrightarrow{\text{Heating}} Ag + CO_2 + \frac{1}{2}O_2$

(e) $\underset{}{CuSO_4.5H_2O} \xrightarrow{100^\circ C} \underset{\text{light greenish blue}}{CuSO_4.H_2O} \xrightarrow{720^\circ C} \underset{\text{Colourless}}{CuSO_4}$

$\xrightarrow{230^\circ C} CuO + SO_2 + \frac{1}{2}O_2$

(f)



$$Hg_2Cl_2 + NH_4OH \longrightarrow Hg\begin{matrix} NH_2 \\ Cl \end{matrix} + \underset{\text{Black}}{Hg}$$

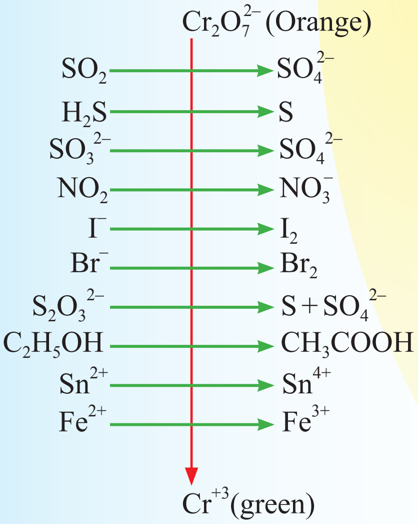
(g) $NO_3^-/NO_2^- \xrightarrow{FeSO_4 + H_2SO_4} \underset{\text{Brown ring complex}}{[Fe(H_2O)_5\ NO^+]SO_4}$

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

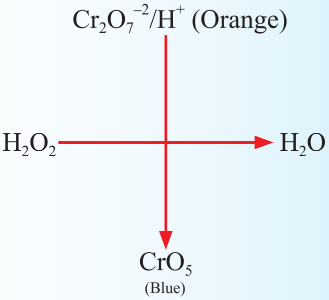
(i) **Chemical volcano:**

$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$

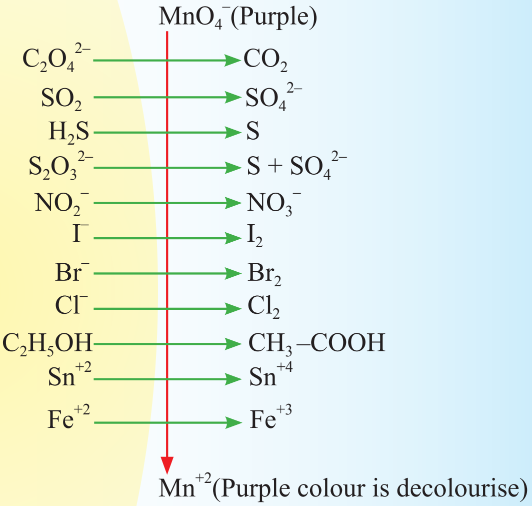
Reactions of $Cr_2O_7^{2-}$



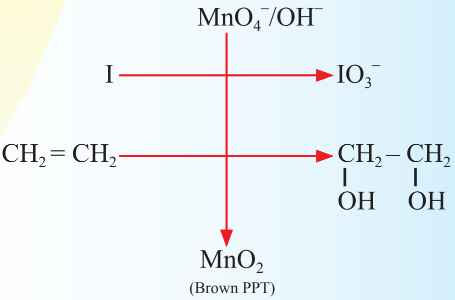
$$\underset{\text{Yellow}}{CrO_4^{2-}} \underset{\bar{O}H}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(Orange)}}{Cr_2O_7^{2-}}$$



Reaction of MnO_4^-



$$\underset{\text{purple}}{MnO_4^-} \xrightarrow[\text{Basic solution}]{\text{Strongly }\Delta} \underset{\text{green}}{MnO_4^{2-}}$$



CHAPTER 30

Coordination Chemistry

Addition compound

(two or more simple salt combining with fixed proportion of mass)

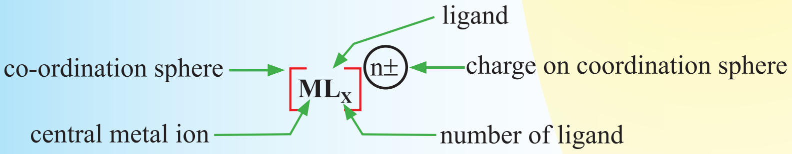
Double salt

- * Loose their identity in aqueous solution
  eg. $KCl.MgCl_2.6H_2O$ carnalite salt
  $K_2SO_4Al_2(SO_4)_3.24H_2O$ potash alum

Co-ordination compound

- * Retain their indentity in aqueous solution
  eg. $K_4[Fe(CN)_6]$ Potassium hexacyanidoferrate (II)

REPRESENTATION OF COMPLEX COMPOUND



Co-ordination number = Number of electron pair accepted by central metal ion.

LIGAND

Chemical species which can donates 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, ox^{2-}, $acac^{-1}$, gly^{-1}, dmg^{-1}

Polydentate (denticity = 2):

eg. dien, trien, $EDTA^{4-}$

Ambidentate : Ligand which have more than one donor site but at the time of donation only atom can donate electron pair.

eg. : (CN^-, NC^-), (NO_2^- , ONO^-), (SCN^-, NCS^-), (OCN^-, NCO^-), ($S_2O_3^{2-}$, SO_2S^{2-})

Flexidentate ligand : Show more than one type of denticity.

eg. : CO_3^{2-}, SO_4^{2-}, CH_3COO^-

NOTES

Bidentate and Polydentate are also called chelating ligand.

Classification on the basis of electron donating and accepting tendency

Classical ligand : H_2O, NH_3 etc.

Non-classical ligand : CN^-, NO^+, NO, CO, PPh_3

π – donor ligand ⇒ C_2H_4, C_2H_2 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.

$$K_4[\overset{+6}{Fe}(CN)_6]$$

$$EAN = 26 - (+2) + 6(2) = 36$$

- 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.

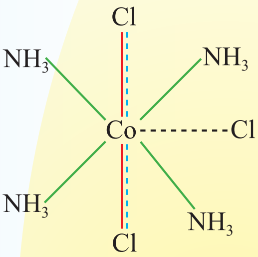
eg.	$[V(CO)_6]$	$[Cr(CO)_6]$	$[Mn(CO)_6]$
	act as oxidising agent	stable complex	act as reducing agent

Brown ring complex	**37**
Sodium nitroprusside	36
Zeise's Salt	84
$Mn_2(CO)_{10}$	36
$Fe_2(CO)_9$	36
$Co_2(CO)_8$	36

WERNER'S CO-ORDINATION THEORY

- Metals possesses two types of valencies PV & SV.
- PV is non-directional, represent by .... (doted line) is satisfied by negative charge species.
- SV is directional, represent by __________ (solid line) and satisfied by negative or neutral species.
- Now a days primary valency and secondary valency is consider as oxidation & co-ordination number respectively.

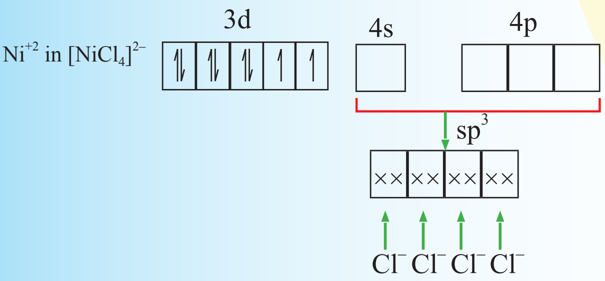
eg. $CoCl_3.4NH_3$
PV = 3, SV = 6
C.N. = 6, Oxidation state = +3



VBT

- Metal provoide hybridised vacant orbital for the acceptance of lone pair from ligand.
- Hybridisation, shape and magnetic behaviour of complex depends upon the nature of ligand.
- Strong field ligand pair up the unpaired e^- of central metal atom where as weak field ligand does not.
- If unpaired e^- present in complex then complex is paramagnetic. If unpaired e^- is absent then diamagnetic.

  eg. CN = 4 ; $[NiCl_4]^{2-}$



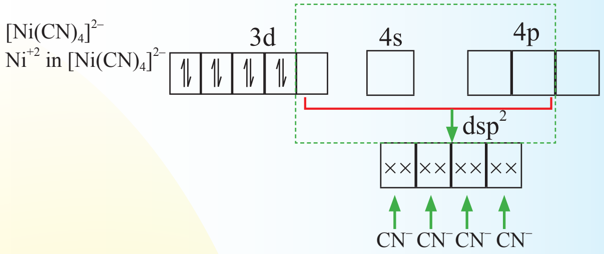
→ Sp^3

→ Tetrahedral

→ Paramagnetic

→ outer Orbital complex

→ $\mu = \sqrt{8}$ BM

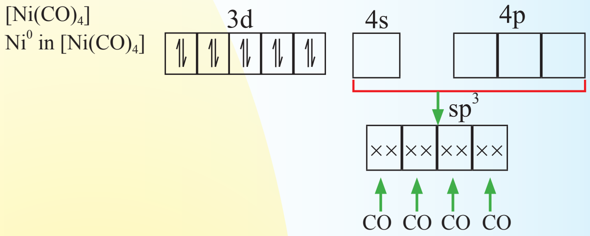


→ dsp^2

→ Square planar

→ Diamagnetic

→ Inner Orbital complex



→ sp^3

→ Tetrahedral

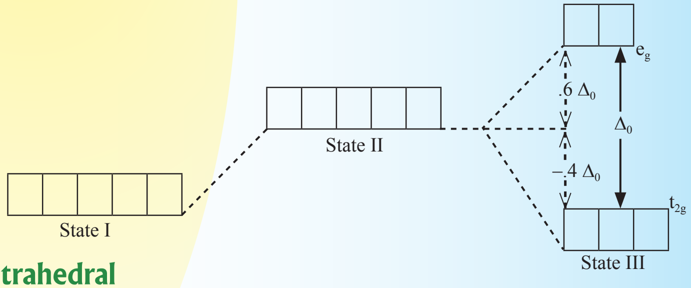
→ Diamagnetic

→ Outer Orbital complex

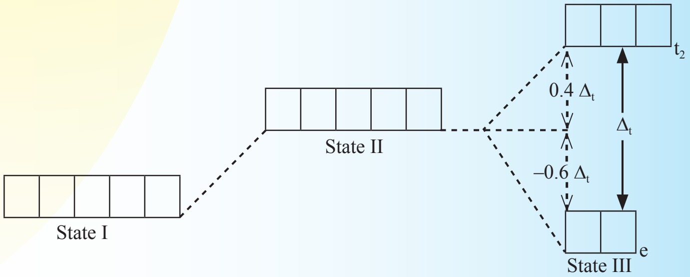
CRYSTAL FIELD THEORY

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

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

Crystal Field Stabilisation Energy (CFSE)

(i) For octahedral CFSE = $[-0.4(n_{t_{2g}}) + 0.6(n_{eg})]\,\Delta_0$ + Paring energy (P.E.) × x

Where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals
n_{eg} = number of electron in eg orbitals
x = number of elctron pair

(ii) For tetrahedral CFSE

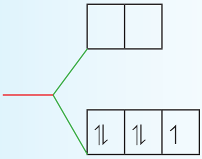
$= [-0.6(n_e) + 0.4\ (n_{t_2})\ \Delta_t$ + Paring energy **(P.E.)** × $x]$

where n_{t_2} = number of electron in t_2 orbitals
n_e = number of electron in e orbitals
x = number of electron pair

⇒ Follow Hund's Pauli & Aufbau rule.

CN-6

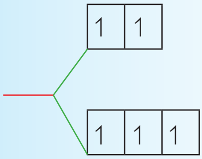
eg. $K_3[Fe(CN)_6]$
Fe^{+3}
CN^- SFL
$\Delta_0 > P$



d^2sp^3, Octahedral low spin complex, inner orbital complex, paramagnetic

$\mu = \sqrt{3}$ BM

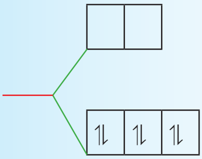
$Fe(F)_6]^{3-}$
Fe^{+3}
F^- WFL
$\Delta_0 < P$



sp^3d^2, Octahedral high spin complex, outer orbital complex, paramagnetic

$\mu = \sqrt{35}$ BM

$[IrF_6]^{3-}$
Ir^{+3}
$\Delta_0 > P$



d^2sp^3, Octahedral low spin complex, inner orbital complex, paramagnetic

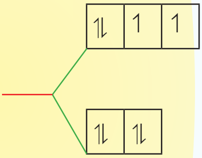
Exception

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

CN-4

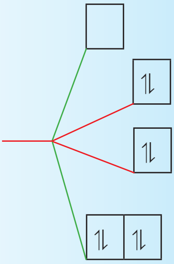
eg.

$[NiCl_4]^{2-}$



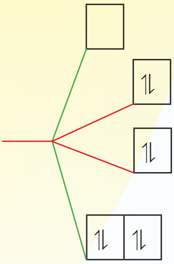
sp^3, Tetrahedral
Outer orbital complex, paramagnetic high spin complex

$[Ni(CN)_4]^{2-}$



dsp^2, Sq. planar
inner orbital complex,
paramagnetic
low spin complex

$[AuCl_4]^-$



dsp^2, Sq. planar
inner orbital complex,
paramagnetic
low spin complex,

Exception

- d^3s hybridisation, Td, diamagnetic, inner orbital complex eg.

  $MnO_4^-, CrO_4^{2-}, Cr_2O_7^{2-}, CrO_2Cl_2, CrO_2F_2, VO_4^{3-}$

- Transference of electron

  eg. Cu^{+2} in CN–4 with L

  (where L = NO_2^- / CN^- / NH_3 etc.)

Factor affecting splitting

(i) Strength of ligand
(ii) Oxidation state of central metal ion
(iii) Transition series (d-series)
(iv) Geometry (number of ligands)
(v) Chelation

Colour of complexes

Colour

d-d transition
→ d^1-d^9 complex can show colour.
→ Complementry colour of absorb colour is observe.
eg. : $[Ti(H_2O_6)]^{3+}$, $[Ni_1(H_2O)_6]^{2+}$ $[Cu(NH)_4]^{2+}$

Charge transfer
→ Metal-metal charge transfers or metal ligand charge transfers
→ MnO_4^-, brown ring complex sodium nitroprusside purssian blue, turnbull's blue

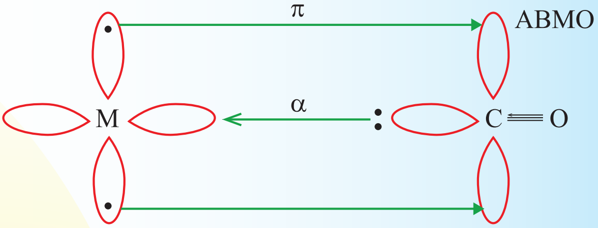
ORGANOMETALLIC COMPOUNDS

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 (O)
- **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 isomersim :** Number of water molecule inside & outside the co-ordinate sphere are different.
  $[Cr(H_2O)_6]Cl_3 \leftrightarrow [Cr(H_2O)_5Cl]Cl_2.H_2O \leftrightarrow [Cr(H_2O)_4Cl_2]Cl.2H_2O$
- **Linkage :** Exihibit 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 :** Exihibit 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 cooridinated 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 com plex $[Mabcd]^{n\pm}$, $[M(AB)cd]^{n\pm}$ $[M(AB)(CD)]^{n\pm}$ show optical isomerism
- Tetrahdral 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

NOTES

Uppercase letter represent chelating ligands and lowercase letter represent monodentate ligands.

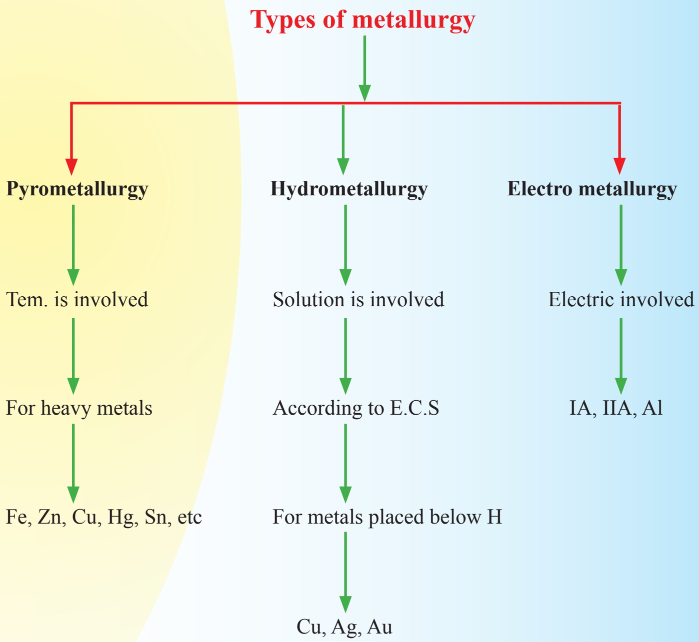
❑❑❑

CHAPTER 31

Metallurgy

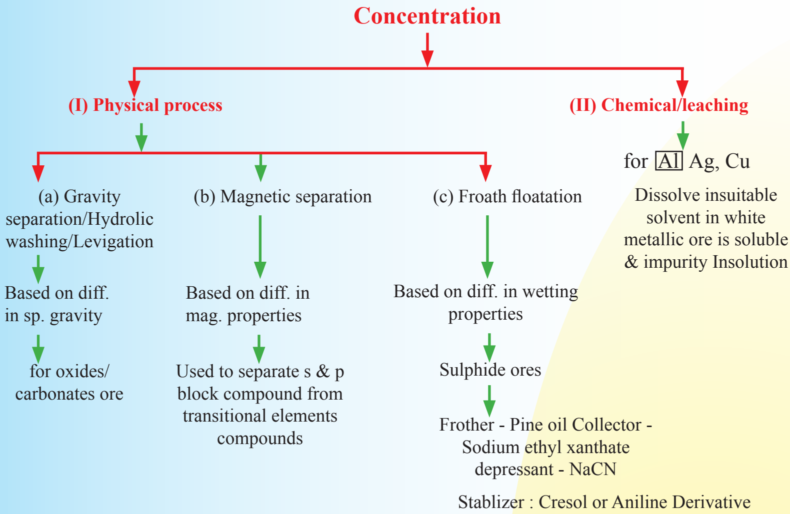
Bunch of Process to Extract Metal from their Respective Ore

Ore : Minerals from which metal can be extracted economically :



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.



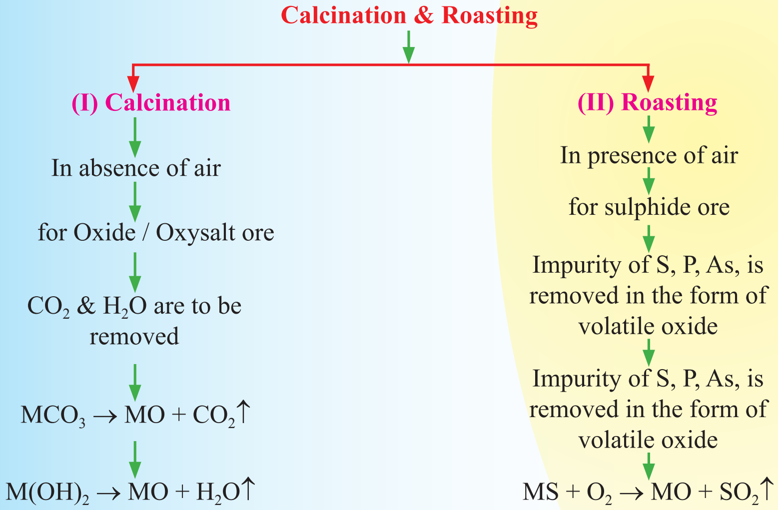
Concentration

- **(I) Physical process**
  - (a) Gravity separation/Hydrolic washing/Levigation
    - Based on diff. in sp. gravity
      - for oxides/ carbonates ore
  - (b) Magnetic separation
    - Based on diff. in mag. properties
      - Used to separate s & p block compound from transitional elements compounds
  - (c) Froath floatation
    - Based on diff. in wetting properties
      - Sulphide ores
        - Frother - Pine oil Collector - Sodium ethyl xanthate depressant - NaCN

          Stablizer : Cresol or Aniline Derivative
- **(II) Chemical/leaching**
  - for $\boxed{\text{Al}}$ Ag, Cu

    Dissolve insuitable solvent in white metallic ore is soluble & impurity Insolution

Ag, Au, are concentrated by cyanide process.



Calcination & Roasting

- **(I) Calcination**
  - In absence of air
    - for Oxide / Oxysalt ore
      - CO_2 & H_2O are to be removed
        - $MCO_3 \rightarrow MO + CO_2\uparrow$
          - $M(OH)_2 \rightarrow MO + H_2O\uparrow$
- **(II) Roasting**
  - In presence of air
    - for sulphide ore
      - Impurity of S, P, As, is removed in the form of volatile oxide
        - Impurity of S, P, As, is removed in the form of volatile oxide
          - $MS + O_2 \rightarrow MO + SO_2\uparrow$

Reduction : To obtains metal (95 to 98%) from metal oxide.

Self reduction

- Sulphide ore itself act as reducing agent.

  eg. $PbS + 2PbO \xrightarrow{\Delta} 2Pb + SO_2$
- Thermal decomposition

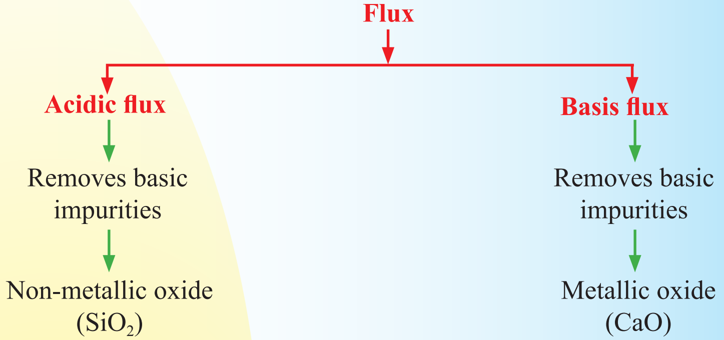
  eg. $HgO \xrightarrow{\Delta} Hg + \frac{1}{2}O_2$

Carbon reduction (Smelting) : Reducing agent C/CO

- eg. $Fe_2O_3 + 3CO \xrightarrow{250^\circ - 700^\circ C} 2Fe + 3CO_2$

  $ZnO + C \xrightarrow{\approx 1200^\circ C} Zn + CO$

Flux - substance to convert non-fusible impurities to fusible one.



Imp. point – Above 710° C is reducing agent.
– Below 710°C CO is better reducing agent.

Aluminum reduction method : (Thermite process)

- Al act as reducing agent

  eg. $Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Cr$

  Thermite mixture mass ratio : $Cr_2O_3 : Al = 3 : 1$

METAL DISPLACEMENT REDUCTION

- Metal placed below H. in E.C.S.
- Ag, Au, Cu

Example of extraction of

(i) Cynidation (Leaching Process)

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

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

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

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

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

ELECTROLYTIC REDUCTION

- For IA, IIA, Al
- Electolysis 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_3AlF_6 & CaF_2 is to added as auxilary electrolytes.

–Na_3AlF_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

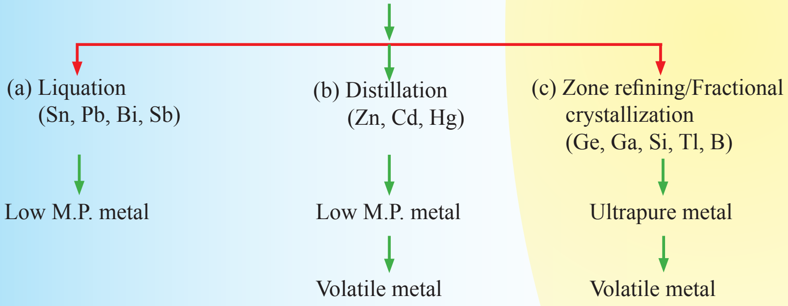
– Down Process Neutral flux ($CaCl_2$) to be added to decrease the fusion temp. of NaCl

– Neutral flux - substance used to increase the conductivity of NaCl

Auxilary 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%)

Refining / Physical Process

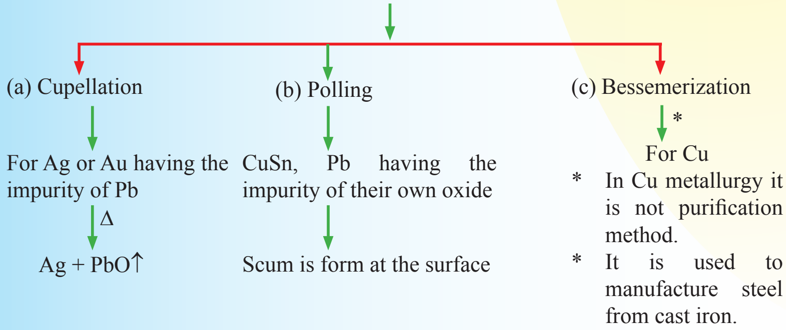


(a) Liquation (Sn, Pb, Bi, Sb) → Low M.P. metal

(b) Distillation (Zn, Cd, Hg) → Low M.P. metal → Volatile metal

(c) Zone refining/Fractional crystallization (Ge, Ga, Si, Tl, B) → Ultrapure metal → Volatile metal

Chemical Process



(a) Cupellation → For Ag or Au having the impurity of Pb $\xrightarrow{\Delta}$ Ag + PbO↑

(b) Polling → CuSn, Pb having the impurity of their own oxide → Scum is form at the surface

(c) Bessemerization →* For Cu

* In Cu metallurgy it is not purification method.

* It is used to manufacture steel from cast iron.

Thermal decomposition (Vapour Phase Refining)

(a) Van arkel de Boer
(Ti, Zr, Hf, B, Th)

Impure metal | Pure metal

$$Ti + I_2 \rightarrow \underset{\text{Volatile}}{TiI_4} \rightarrow \overset{\text{Pure}}{Ti} + 2I_2$$

Impurity + I_2 → No reaction
(Or not form volatile product)

(a) Mondi's process
(for Ni)

$$Ni + 4CO \xrightarrow{\Delta} \underset{\text{Volatile carbonyl}}{Ni(CO)_4} \xrightarrow{\Delta} \underset{\text{(Pure metal)}}{Ni + 4CO}$$

Impurity + CO → 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 $E^o = -1.66$	1. Bauxite, $Al_2O_3.xH_2O$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten $Na_3AlF_6 + CaF_2$	Electrolytic refining by Hoop's cell	For the extraction, a good source of electricity is required

Metal	Occurrence	Common method of extraction	Reffining	Remarks
Iron $E^o = -0.44$	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4 3. Limonite, $Fe_2O_3.3H_2O$ 4. Siderite, $FeCO_3$	Reduction of the oxide with CO and coke in Blast furnace	Bessemerization (impurites has more affinity for O_2 as compare to Fe)	Temperature approaching 2170K is required
Copper $E^o = -0.34$	1. Copper pyrites, $CuFeS_2$ 2. Copper glance, Cu_2S 3. Malachite, $CuCO_3.Cu(OH)_2$ 4. Cuprite, Cu_2O 5. Azurite, $2CuCO_3.Cu(OH)_2$	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 $E^o = -0.76$	1. Zinc blende or Sphalerite, ZnS 2. Calamine, $ZnCO_3$ 3. Zincite, ZnO	Roasting of sulphide ore or calcination of $ZnCO_3$ followed by reduction with coke	The metal may be purifed by fractional distillation	For ZnO, carbon is better reducing agent then CO and Zn is obtain is vapours form $ZnO + C \xrightarrow{1673K} Zn + CO$
Mg $E^o = -2.36$	1. Carnallite, $KCl.MgCl_2.6H_2O$ 2. Magnesite, $MgCO_3$	Electrolysis of fused $MgCl_2$ with KCl		$MgCl_2.6H_2O$ is heated in the excess current of dry HCl gas to produce anhydrous $MgCl_2$
Sn $E^o = -0.14$	1. Cassiterite, SnO_2 (Tin stone)	Reduction of the SnO_2 with carbon. $SnO_2 + 2C \rightarrow Sn + 2CO$	Polling and Liquidation	Ore contain impurity of wolframite, $FeWO_4 + MnWO_4$ (magnetic sepration)

Metal	Occurrence	Common method of extraction	Reffining	Remarks
Pb E° = –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° = 0.80	1. Argentite- Ag_2S, native Silver	Hydro metallurgy $Ag_2S + 4NaCN$ $2NaAg(CN)_2 + N_2S$ $2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Ag$	Cupelation & electrolytic method	In hydro mettallurgy Ag obtain in the form of dark amorphous ppt.
Au E° = 1.40	Native ore	1. Amalgamation. 2. Cynide process	Cupelation & electrolysis method.	In hydro mettallurgy Au obtain in the form of dark amorphous ppt.

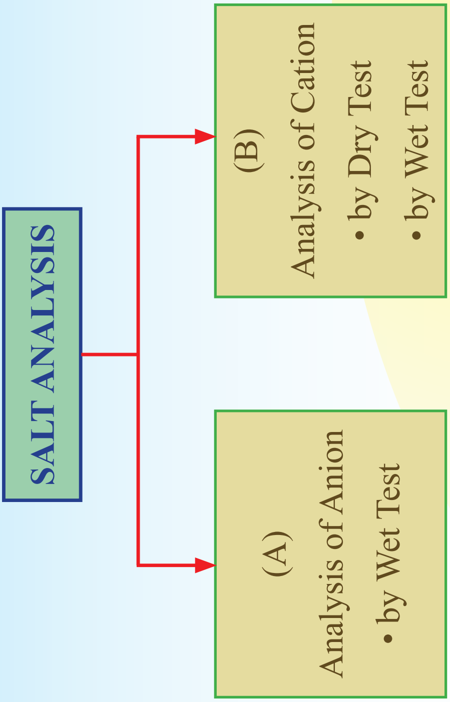
CHAPTER 32

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_2SO_4) CO_3^{2-}, HCO_3^-, SO_3^{2-}, HSO_3^-, $S_2O_3^{2-}$, S^{2-}, CH_3COO^-, 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_2SO_4) F^-, Cl^-, Br^-, I^-, NO_3^-, BO_3^{3-}, $C_2O_4^{2-}$ + sub group-I	(Detected by redox reaction) CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, MnO_4^{-2}

- CO_2 is colourless, odourless gas evolved with brisk effevescence, Detected by lime water test.
- So_2 is colourless, Suffocating gas with burning sulphur odour. Detected by lime water test or by passing in $Cr_2O_7^{2-}/H^+$ solution.
- H_2S is a colourless gas having rotten egg odour.
- CH_3COOH has colourless fumes having vinegar odour.
- NO_2/Br_2 is brown gas.
- I_2 is violet gas.

LIME WATER / BARYTA WATER TEST

When CO_2 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 CO_2 is passed then white turbidity disappeared due to formation of soluble bicarbonate.

$$CO_2\uparrow + Ca^{2+} + 2OH^- \rightarrow \underset{\text{White turbidity}}{CaCO_3\downarrow} + H_2O$$

$$CaCO_3\downarrow + CO_2\uparrow + H_2O \rightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

NOTES

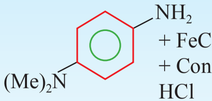
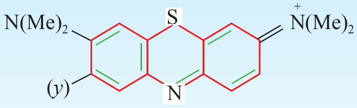
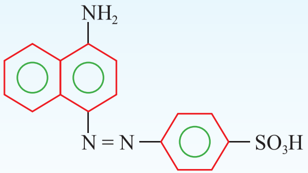
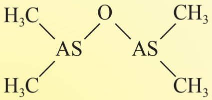
SO_2 also gives similar observation.

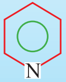
ACIDIC RADICAL TABLE

	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	$HgCO_3 . 3HgO\downarrow$ Reddish brown	$Ag_2CO_3\downarrow$	$PbCO_3 .$ $2Pb(OH)_2\downarrow$	–
$HCO_3^- + \Delta$	$CO_2\uparrow$	$CO_2\uparrow$	$CaCO_3\downarrow$	$BaCO_3\downarrow$	$HgCO_3 . 3HgO\downarrow$ Reddish brown	$Ag_2CO_3\downarrow$	$PbCO_3 .$ $2Pb(OH)_2\downarrow$	–
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$_2$	$BaCl_2$	$HgCl_2$	$AgNO_3$	$Pb(OAc)_2$	MnO_4^-/H^+
Cl^-		$HCl\uparrow$	–	–	–	$AgCl\downarrow$ white	$PbCl_2\downarrow$ white	$Cl_2\uparrow$
Br^-		$Br_2\uparrow$ brown	–	–	–	$AgBr\downarrow$ pale yellow	$PbBr_2\downarrow$ white	$Br_2\uparrow$
$C_2O_4^{2-}$	–	$CO_2\uparrow + CO\uparrow$	$CaC_2O_4\downarrow$ white	$BaC_2O_4\downarrow$ white	–	$Ag_2C_2O_4\downarrow$ white	–	$CO_2\uparrow$
BO_2^-	–	$H_3BO_3\uparrow$	$Ca(BO_2)\downarrow$ white	$Ba(BO_2)\downarrow$ white	–	$AgBO_2\downarrow$ white	–	–
NO_3^-	–	$NO_2\uparrow$	–	–	–	–	–	–
SO_4^{2-}	–	–	$CaSO_4\downarrow$ white	$BaSO_4\downarrow$ curdy white ppt	$HgSO_4.2HgO\downarrow$ yellow	–	$PbSO_4\downarrow$ white	–
PO_4^{3-}	–	–	$CaHPO_4\downarrow$ white	$BaHPO_4\downarrow$ white	–	$Ag_3PO_4\downarrow$ yellow	–	–
CrO_4^{2-}	–	–	–	$BaCrO_4\downarrow$ yellow	–	$Ag_2CrO_4\downarrow$ brick red	$PbCrO_4\downarrow$ yellow	–

SPECIFIC REACTION OF ACIDIC RADICAL

Anion	Reaction Nmae /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	 $+ FeCl_3$ $+$ Conc. HCl	 $+Fe + Cl$	Methylene Blue
NO_2^-	Gries Illosavay Test	(i) Sulphanilic acid (ii) 1, Methyl Amine		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		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	$FeSO_4$ + Conc. H_2SO_4	$[Fe(H_2O)_5NO]SO_4$	Brown Ring
$C_2O_4^{2-}$	Mn^{+2} + NaOH	$NaOH + Mn^{+2} \xrightarrow{\Delta}$	$[Mn(C_2O_4)_3]^{3-}$	Red Complex
Br^-	Layer Test	Cl_2 Water + CCl_4	$Br_2 + CCl_4$	Red layer
I^-	Layer Test	Cl_2 Water + CCl_4	$I_2 + CCl_4$	Violet Layer
I^-	$HgCl_2$	$HgCl_2$	HgI_2	Red/yellow
Cl^-	Chromyl Chloride Test	(i) $K_2Cr_2O_7(s)$ + conc. H_2SO_4 (ii) NaOH (iii) $Pb(CH_3COO)_2$ + CH_3COOH	CrO_2Cl_2 CrO_4^{2-} ↓ $PbCrO_4$	Reddish brown Vapour ↓ Yellow Solution ↓ Yellow PPt.
BO_3^{3-}	Green Flame Test	Conc. H_2SO_4 + ROH + Δ(Flame)	$B(OR)_3$	Green edge flame
BO_3^{3-}	Modified Green Flame Test	CaF_2 + Conc. H_2SO_4	$BF_3\uparrow + Ca(HSO_4)_2 + \Delta$	Green flame
PO_4^{3-}	Ammonium molybdate	$(NH_4)_2MoO_4$ + dil HNO_3 + 30 – 40° C	$Na_3MoO_4.12MoO_3$	Canary yellow ppt.
$Cr\,O_4^{2-}$/ Cr_2O_7	Acidic Solution of H_2O_2 + pyridine	$H_2O_2 + H^+ +$ 	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)	Caramine 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

Charcol 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. $Co(No_3)_2$ and heat.

Zn^{+2}	$ZnO.CoO$	Rinmann's Green
Al^{+3}	Al_2O_3	Thenard Blue
Mg^{+2}	$MgO.CoO$	Pink residue
Sn^{+2}	$SnO.CoO$	Bluish residue

CLASSIFICATION OF BASIC RADICAL

Group	**Basic Radical**	**Reagent used**	**Precipitate form**
Group-I	Pb^{+2}, Hg_2^{+2}	dil HCl	$\underbrace{AgCl \quad PbCl_2 \quad Hg_2Cl_2}_{\text{white ppt.}}$
Group-II	Cu^{+2}, Pb^{+2}, Hg^{+2}, Cd^{+2}, Bi^{+3}	H_2S+dil. HCl	$\underbrace{Cu_2S,\ PbS,\ HgS}_{\text{Black}}$, CdS, Bi_2S_3 yellow black
	Sn^{+2}, Sn^{+4}, As^{+3}, As^{+5}, Sb^{+3}, Sb^{+5}		SnS Brown SnS_2 Brown $\underbrace{As_2S_3As_2S_5}_{\text{yellow}}$ $\underbrace{Sb_2S_3Sb_2S_5}_{\text{Gray}}$
Group-III	Cr^{+3}, Al^{+3}, Fe^{+3}	NH_4OH + NH_4Cl	$Al(OH)_{3+}$ gelatinous white $Fe(OH)_3$, reddish brown $Cr(OH)_3$ green
Group-IV	Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}	H_2S + NH_4OH	ZnS white MnS buff $\underbrace{NiS \quad CoS}_{\text{black}}$
Group-V	Ca^{+2}, Sr^{+2}, Ba^{+2}	$(NH_4)_2CO_3$ + NH_4OH	$\underbrace{CaCO_3,\ SrCO_3,\ BaCO_3}_{\text{white}}$

TEST OF BASIC RADICAL

	Ag^+	Hg_2^{2+}	Pb^{2+}	Cu^{+2}	Hg^{+2}	Cd^{+2}	Al^{+3}
KI	AgI Yellow	Hg_2I_2 Green	PbI_2 Yellow	$CuI + I_3^-$ White solution	HgI_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	$CuCN + [CN]_2\uparrow$	—	$Cd(CN)_2$ White	—
ex KCN	$[Ag(CN)_2]^-$	—	—	$K_3[Cu(CN)_4]$ soluble complex	—	$[Cd(CN)_4]^2$	—
NaOH	Ag_2O Brown	Hg_2O 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	$Hg + HgO.$ $HgNH_2^+NO_3$	$Pb(OH)_2$ White	$Cu(OH)_2$ Pale Blue	HgO. $HgNH_2Cl$ White	$Cd(OH)_2$ White	$Al(OH)_3$ Gelatinous white
ex NH_4OH	$[Ag(NH_3)_2]^+$	—	—	$[Cu(NH_3)_4]^{2+}$ Deep blue	—	$[Cd(NH_3)_4]^{2+}$	—
$H_2S/^*(NH_4)_2S$	Ag_2S Black	$\underbrace{Hg + HgS}_{\text{black}}$	PbS Back	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	—	—	—	—
$Na_2S_2O_3$	$Ag_2S_2O_3$ White	—	PbS_2O_3 White	$Cu_2S_2O_3$ White	HgS_2O_3 White	—	—
$K_4[Fe(CN)_6]$	$Ag_4[Fe(CN)_6]$ White	—	—	$Cu_2[Fe(CN)_6]$ Brown	—	—	—
$K_3[Fe(CN)_6]$	—	—	—	$Cu_3[Fe(CN)_6]$ Green	—	—	—

TEST OF BASIC RADICAL

	Cr^{+3}	Fe^{+3}	Fe^{+2}	Zn^{+2}	Mn^{+2}	Ni^{+2}	Co^{+2}
KI	—	$FeI_2 + I_3^-$ 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	—	$K_3[Fe(CN)_6]$ Yellow	$K_4[Fe(CN)_6]$ Pale yellow	—	—	$K_2[Ni(CN)_4]$ Soluble Complex	$[Co(CN)6]^{-4}$ 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	$Na[(AlOH)_4]$ Yellow	—	—	$Na_2[Zn(OH)_4]$	—	—	$(CoOH)_2$ pink
NH_4OH	$Cr(OH)_3$ 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_4OH	$[Cr(NH_3)_6]^{3+}$ Pink/vollet	—	—	$[Zn(NH_3)_4]^{2+}$	—	$Ni[(NH_3)_6]^{2+}$ Deep blue	$[Co(NH_3)_6]^{2+}$ Yellow
H_2S/*$(NH_4)_2S$	$Cr(OH)_3$ Green	$FeS + S$ Black yellow	FeS Black	ZnS White	MnS Pink	NiS Black	CoS Black
K_2CrO_4	—	—	—	—	—	—	—
$Na_2S_2O_3$	—	Fe^{+2} Green solution					
$K_4[Fe(CN)_6]$	—	$Fe_4[Fe(CN_6)]_3$ Prussian blue	$K_2Fe[Fe(CN)_6]$	$K_2Zn_3[Fe(CN)_6]$ 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^-	$Fe(SCN)_3$	Blood red colcuration
Ni^{+2}	dmg / $NH4^+$	$[Ni(dmg)_2]$	Rosy red complex
Co^{+2}	KNO_2	$K_3[Co(NO_2)_6]$	Yellow ppt
Hg^{+2}	$SnCl_2$(ex)	Hg	Grey / black
K^+	$HClO_4$	$KClO_4$	White ppt