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PHYSICAL CHEMISTRY

ATOMIC STRUCTURE

Planck's Quantum Theory :

$$\text{Energy of one photon} = h\nu = \frac{hc}{\lambda}$$

Photoelectric Effect :

$$h\nu = h\nu_0 + \frac{1}{2}m_e v^2$$

Bohr's Model for Hydrogen like atoms :

1. $mvr = n \frac{h}{2\pi}$ (Quantization of angular momentum)

2. $E_n = -\frac{E_1}{n^2}$ $z^2 = -2.178 \times 10^{-18} \frac{z^2}{n^2}$ J/atom = $-13.6 \frac{z^2}{n^2}$ eV

$$E_1 = \frac{-2\pi^2 me^4}{n^2}$$

3. $r_n = \frac{n^2}{Z} \frac{h^2}{4\pi^2 e^2 m} = \frac{0.529 \times n^2}{Z} \text{ \AA}$

4. $v = \frac{2\pi z e^2}{nh} = \frac{2.18 \times 10^6 \times z}{n}$ m/s

De Broglie wavelength :

$$\lambda = \frac{h}{mc} = \frac{h}{p} \text{ (for photon)}$$

Wavelength of emitted photon :

$$\frac{1}{\lambda} = \nu = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

No. of photons emitted by a sample of H atom :

$$\frac{\Delta n(\Delta n + 1)}{2}$$

Heisenberg's uncertainty principle :

$$\Delta x \cdot \Delta p > \frac{h}{4\pi} \quad \text{or} \quad m \Delta x \cdot \Delta v \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

Quantum Numbers :

- * Principal quantum number (n) = 1, 2, 3, 4..... to ∞ .
- * Orbital angular momentum of electron in any orbit = $\frac{nh}{2\pi}$.
- * Azimuthal quantum number (ℓ) = 0, 1, to $(n - 1)$.
- * Number of orbitals in a subshell = $2\ell + 1$
- * Maximum number of electrons in particular subshell = $2 \times (2\ell + 1)$
- * Orbital angular momentum $L = \frac{h}{2\pi} \sqrt{\ell(\ell+1)} = \sqrt{\ell(\ell+1)}$

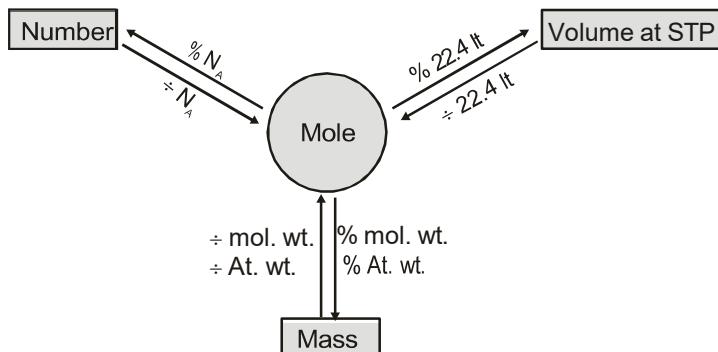
$$\left[L = \frac{h}{2\pi} \right]$$

STOICHIOMETRY

Relative atomic mass (R.A.M) = $\frac{\text{Mass of one atom of an element}}{\frac{1}{12} \times \text{mass of one carbon atom}}$

= Total Number of nucleons

Y-map



Density :

$$\text{Specific gravity} = \frac{\text{density of the substance}}{\text{density of water at } 4^\circ\text{C}}$$

For gases :

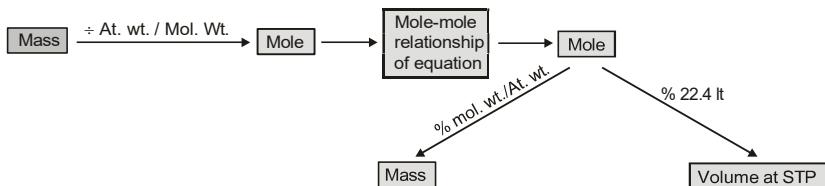
$$\text{Absolute density (mass/volume)} = \frac{\text{Molar mass of the gas}}{\text{Molar volume of the gas}}$$

$$\Rightarrow \rho = \frac{PM}{RT}$$

$$\text{Vapour density} \quad V.D. = \frac{d_{\text{gas}}}{d_{\text{H}_2}} = \frac{PM_{\text{gas}}/RT}{PM_{\text{H}_2}/RT} = \frac{M_{\text{gas}}}{M_{\text{H}_2}} = \frac{M_{\text{gas}}}{2}$$

$$M_{\text{gas}} = 2 \text{ V.D.}$$

Mole-mole analysis :



Concentration terms :

Molarity (M) :

$$\therefore \text{Molarity (M)} = \frac{w \times 1000}{(\text{Mol. wt of solute}) \times V_{\text{in ml}}}$$

Molality (m) :

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{mass of solvent in gram}} \times 1000 = \frac{1000 w}{M w}$$

Mole fraction (x) :

$$\therefore \text{Mole fraction of solution (x}_1\text{)} = \frac{n}{n+N}$$

$$\therefore \text{Mole fraction of solvent (x}_2\text{)} = \frac{N}{n+N}$$

$$x_1 + x_2 = 1$$

% Calculation :

$$(i) \text{ } \% \text{ w/w} = \frac{\text{mass of solute in gm}}{\text{mass of solution in gm}} \times 100$$

$$(ii) \text{ } \% \text{ w/v} = \frac{\text{mass of solute in gm}}{\text{Volume of solution in ml}} \times 100$$

$$(iii) \text{ } \% \text{ v/v} = \frac{\text{Volume of solute in ml}}{\text{Volume of solution}} \times 100$$

Derive the following conversion :

$$1. \text{ Mole fraction of solute into molarity of solution } M = \frac{x_2 \rho \times 1000}{x_1 M_1 + M_2 x_2}$$

$$2. \text{ Molarity into mole fraction } x_2 = \frac{M M_1 \times 1000}{\rho \times 1000 - M M_2}$$

$$3. \text{ Mole fraction into molality } m = \frac{x_2 \times 1000}{x_1 M_1}$$

$$4. \text{ Molality into mole fraction } x_2 = \frac{m M_1}{1000 + m M_1}$$

$$5. \text{ Molality into molarity } M = \frac{m \rho \times 1000}{1000 + m M_2}$$

$$6. \text{ Molarity into Molality } m = \frac{M \times 1000}{1000 \rho - M M_2}$$

M_1 and M_2 are molar masses of solvent and solute. ρ is density of solution (gm/mL)

M = Molarity (mole/lit.), m = Molality (mole/kg), x_1 = Mole fraction of solvent, x_2 = Mole fraction of solute

Average/Mean atomic mass :

$$A_x = \frac{a_1 x_1 + a_2 x_2 + \dots + a_n x_n}{100}$$

Mean molar mass or molecular mass :

$$M_{\text{avg.}} = \frac{n_1 M_1 + n_2 M_2 + \dots + n_n M_n}{n_1 + n_2 + \dots + n_n} \quad \text{or} \quad M_{\text{avg.}} = \frac{\sum_{j=1}^{j=n} n_j M_j}{\sum_{j=1}^{j=n} n_j}$$

Calculation of individual oxidation number :

Formula : Oxidation Number = number of electrons in the valence shell
– number of electrons left after bonding

Concept of Equivalent weight/Mass :

For elements, equivalent weight (E) =
$$\frac{\text{Atomic weight}}{\text{Valency - factor}}$$

For acid/base,
$$E = \frac{M}{\text{Basicity / Acidity}}$$

Where M = Molar mass

For O.A/R.A,
$$E = \frac{M}{\text{no. of moles of } e^- \text{ gained/lost}}$$

Equivalent weight (E) =
$$\frac{\text{Atomic or molecular weight}}{\text{v.f.}}$$

(v.f. = valency factor)

Concept of number of equivalents :

No. of equivalents of solute =
$$\frac{Wt}{\text{Eq. wt.}} = \frac{W}{E} = \frac{W}{M/n}$$

No. of equivalents of solute = No. of moles of solute % v.f.

Normality (N) :

Normality (N) =
$$\frac{\text{Number of equivalents of solute}}{\text{Volume of solution (in litres)}}$$

Normality = Molarity % v.f.

Calculation of valency Factor :

n-factor of acid = basicity = no. of H^+ ion(s) furnished per molecule of the acid.

n-factor of base = acidity = no. of OH^- ion(s) furnished by the base per molecule.

At equivalence point :

$$N_1 V_1 = N_2 V_2$$
$$n_1 M_1 V_1 = n_2 M_2 V_2$$

Volume strength of H_2O_2 :

20V H_2O_2 means **one litre** of this sample of H_2O_2 on decomposition gives **20 Lt. of O_2 gas at S.T.P.**

$$\text{Normality of } \text{H}_2\text{O}_2 (N) = \frac{\text{Volume, strength of } \text{H}_2\text{O}_2}{5.6}$$

$$\text{Molarity of } \text{H}_2\text{O}_2 (M) = \frac{\text{Volume strength of } \text{H}_2\text{O}_2}{11.2}$$

Measurement of Hardness :

$$\text{Hardness in ppm} = \frac{\text{mass of } \text{CaCO}_3}{\text{Total mass of water}} \times 10^6$$

Calculation of available chlorine from a sample of bleaching powder :

$$\% \text{ of } \text{Cl}_2 = \frac{3.55 \times x \times V(\text{mL})}{W(\text{g})} \text{ where } x = \text{molarity of hypo solution}$$

and v = mL. of hypo solution used in titration.

GASEOUS STATE

Temperature Scale :

$$\frac{\text{C} - \text{O}}{100 - 0} = \frac{\text{K} - 273}{373 - 273} = \frac{\text{F} - 32}{212 - 32} = \frac{\text{R} - \text{R(O)}}{\text{R}(100) - \text{R(O)}}$$

where R = Temp. on unknown scale.

Boyle's law and measurement of pressure :

$$\text{At constant temperature, } V \propto \frac{1}{P}$$
$$P_1 V_1 = P_2 V_2$$

Charles law :

$$\text{At constant pressure, } V \propto T \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Gay-lussac's law :

$$\text{At constant volume, } P \propto T \quad \frac{P_1}{T_1} = \frac{P_2}{T_2} \rightarrow \text{temp on absolute scale}$$

Ideal gas Equation :

$$PV = nRT$$

$$PV = \frac{w}{m} RT \text{ or } P = \frac{d}{m} RT \text{ or } Pm = dRT$$

Daltons law of partial pressure :

$$P_1 = \frac{n_1 RT}{V}, \quad P_2 = \frac{n_2 RT}{V}, \quad P_3 = \frac{n_3 RT}{V} \text{ and so on.}$$

$$\text{Total pressure} = P_1 + P_2 + P_3 + \dots$$

Partial pressure = mole fraction \times Total pressure.

Amagatís law of partial volume :

$$V = V_1 + V_2 + V_3 + \dots$$

Average molecular mass of gaseous mixture :

$$M_{\text{mix}} = \frac{\text{Total mass of mixture}}{\text{Total no. of moles in mixture}} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3}$$

Grahamís Law :

$$\text{Rate of diffusion } r \propto \frac{1}{\sqrt{d}}; \quad d = \text{density of gas}$$

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \sqrt{\frac{V \cdot D_2}{V \cdot D_1}}$$

Kinetic Theory of Gases :

$$PV = \frac{1}{3} m N \overline{U^2} \quad \text{Kinetic equation of gases}$$

$$\text{Average K.E. for one mole} = N_A \left(\frac{1}{2} m \overline{U^2} \right) = \frac{3}{2} K N_A T = \frac{3}{2} RT$$

☞ Root mean square speed

$$U_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad \text{molar mass must be in kg/mole.}$$

☞ Average speed

$$U_{\text{av}} = U_1 + U_2 + U_3 + \dots + U_N$$

$$U_{\text{avg.}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8KT}{\pi m}} \quad K \text{ is Boltzmann constant}$$

☞ Most probable speed

$$U_{\text{MPS}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2KT}{m}}$$

Van der Waal's equation :

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

☞ Critical constants :

$$V_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27Rb}$$

THERMODYNAMICS

Thermodynamic processes :

1. **Isothermal process :** $T = \text{constant}$
 $dT = 0$
 $\Delta T = 0$
2. **Isochoric process :** $V = \text{constant}$
 $dV = 0$
 $\Delta V = 0$
3. **Isobaric process :** $P = \text{constant}$
 $dP = 0$
 $\Delta P = 0$
4. **Adiabatic process :** $q = 0$
or heat exchange with the surrounding = 0(zero)

IUPAC Sign convention about Heat and Work :

Work done on the system = Positive

Work done by the system = Negative

1st Law of Thermodynamics

$$\Delta U = (U_2 - U_1) = q + w$$

Law of equipartition of energy :

$$U = \frac{f}{2} nRT \quad (\text{only for ideal gas})$$

$$\Delta E = \frac{f}{2} nR (\Delta T)$$

where f = degrees of freedom for that gas. (Translational + Rotational)

$f = 3$ for monoatomic

$= 5$ for diatomic or linear polyatomic

$= 6$ for non - linear polyatomic

Calculation of heat (q) :

Total heat capacity :

$$C = \frac{\Delta q}{T} = \frac{dq}{\Delta T} = J/EC$$

Molar heat capacity :

$$C = \frac{\Delta q}{n\Delta T} = \frac{dq}{n\Delta T} = J \text{ mole}^{-1} \text{ K}^{-1}$$

$$C_p = \frac{\gamma R}{\gamma - 1} \quad C_v = \frac{R}{\gamma - 1}$$

Specific heat capacity (s) :

$$S = \frac{\Delta q}{m\Delta T} = \frac{dq}{m\Delta T} = J \text{ gm}^{-1} \text{ K}^{-1}$$

WORK DONE (w) :

Isothermal Reversible expansion/compression of an ideal gas :

$$W = -nRT \ln (V_f/V_i)$$

Reversible and irreversible isochoric processes.

$$\text{Since } dV = 0$$

$$\text{So } dW = -P_{\text{ext}} \cdot dV = 0.$$

Reversible isobaric process :

$$W = P (V_f - V_i)$$

Adiabatic reversible expansion :

$$\Rightarrow T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

Reversible Work :

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} = \frac{nR (T_2 - T_1)}{\gamma - 1}$$

Irreversible Work :

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} = \frac{nR (T_2 - T_1)}{\gamma - 1} = nC_v (T_2 - T_1) = -P_{\text{ext}} (V_2 - V_1)$$

$$\text{and use } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Free expansion Always going to be irreversible and since $P_{\text{ext}} = 0$
so $dW = -P_{\text{ext}} \cdot dV = 0$
If no. heat is supplied $q = 0$
then $\Delta E = 0$ so $\Delta T = 0$.

Application of 1st Law :

$$\Delta U = \Delta Q + \Delta W \Rightarrow \Delta W = -P \Delta V$$
$$\therefore \Delta U = \Delta Q - P \Delta V$$

Constant volume process

Heat given at constant volume = change in internal energy

$$\therefore dU = (dq)_v$$

$$dU = nC_v dT$$

$$C_v = \frac{1}{n} \cdot \frac{dU}{dT} = \frac{f}{2} R$$

Constant pressure process :

H = Enthalpy (state function and extensive property)

$$H = U + PV$$

$$\Rightarrow C_p \neq C_v = R \text{ (only for ideal gas)}$$

Second Law Of Thermodynamics :

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \quad \text{for a spontaneous process.}$$

Entropy (S) :

$$\Delta S_{\text{system}} = \int_A^B \frac{dq}{T_{\text{env}}}$$

Entropy calculation for an ideal gas undergoing a process :

$$\text{State A} \xrightarrow[\Delta S_{\text{irr}}]{\text{r}} \text{State B}$$

$$P_1, V_1, T_1 \qquad \qquad \qquad P_2, V_2, T_2$$

$$\Delta S_{\text{system}} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad \text{(only for an ideal gas)}$$

Third Law Of Thermodynamics :

The entropy of perfect crystals of all pure elements & compounds is zero at the absolute zero of temperature.

Gibbís free energy (G) : (State function and an extensive property)

$$G_{\text{system}} = H_{\text{system}} - TS_{\text{system}}$$

Criteria of spontaneity :

- (i) If ΔG_{system} is $(-\text{ve}) < 0$ \Rightarrow process is spontaneous
- (ii) If ΔG_{system} is > 0 \Rightarrow process is non spontaneous
- (iii) If $\Delta G_{\text{system}} = 0$ \Rightarrow system is at equilibrium.

Physical interpretation of ΔG :

→ The maximum amount of non-expansional (compression) work which can be performed.

$$\Delta G = dw_{\text{non-exp}} = dH - TdS.$$

Standard Free Energy Change (ΔG°) :

1. $\Delta GE = -2.303 RT \log_{10} K$
2. At equilibrium $\Delta G = 0$.
3. The decrease in free energy ($-\Delta G$) is given as :

$$-\Delta G = W_{\text{net}} = 2.303 nRT \log_{10} \frac{V_2}{V_1}$$

4. ΔG_f° for elemental state = 0
5. $\Delta G_f^\circ = G_{\text{products}}^\circ - G_{\text{Reactants}}^\circ$

Thermochemistry :

Change in standard enthalpy $\Delta HK = H_{m,2}^\circ - H_{m,1}^\circ$

= heat added at constant pressure.

$$= C_p \Delta T.$$

If $H_{\text{products}} > H_{\text{reactants}}$

→ Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products

and if $H_{\text{products}} < H_{\text{reactants}}$

→ Reaction will be exothermic as extra heat content of reactants will be released during the reaction.

Enthalpy change of a reaction :

$$\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$$

$$\Delta HK_{\text{reactions}} = HK_{\text{products}} - HK_{\text{reactants}}$$

= positive – endothermic

= negative – exothermic

Temperature Dependence Of ΔH : (Kirchoff's equation) :

For a constant pressure reaction

$$\Delta H_2 K = \Delta H_1 K + \Delta C_p (T_2 - T_1)$$

where $\Delta C_p = C_p(\text{products}) - C_p(\text{reactants})$.

For a constant volume reaction

$$\Delta E_2^\circ = \Delta E_1^\circ + \int \Delta C_V \cdot dT$$

Enthalpy of Reaction from Enthalpies of Formation :

The enthalpy of reaction can be calculated by

$$\Delta H_r K = \sum v_B \Delta H_f K_{\text{products}} - \sum v_B \Delta H_f K_{\text{reactants}}$$

v_B is the stoichiometric coefficient.

Estimation of Enthalpy of a reaction from bond Enthalpies :

$$\Delta H = \left(\begin{array}{l} \text{Enthalpy required to} \\ \text{break reactants into} \\ \text{gasesous atoms} \end{array} \right) - \left(\begin{array}{l} \text{Enthalpy released to} \\ \text{form products from the} \\ \text{gasesous atoms} \end{array} \right)$$

Resonance Energy :

$$\begin{aligned} \Delta H K_{\text{resonance}} &= \Delta H K_f, \text{experimental} - \Delta H K_f, \text{calculated} \\ &= \Delta H K_c, \text{calculated} - \Delta H K_c, \text{experimental} \end{aligned}$$

CHEMICAL EQUILIBRIUM

At equilibrium :

- (i) Rate of forward reaction = rate of backward reaction
- (ii) Concentration (mole/litre) of reactant and product becomes constant.
- (iii) $\Delta G = 0$.
- (iv) $Q = K_{\text{eq}}$.

Equilibrium constant (K) :

$$K = \frac{\text{rate constant of forward reaction}}{\text{rate constant of backward reaction}} = \frac{K_f}{K_b}.$$

Equilibrium constant in terms of concentration (K_c) :

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

Equilibrium constant in terms of partial pressure (K_p) :

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

Equilibrium constant in terms of mole fraction (K_x) :

$$K_x = \frac{x_c x_d}{x_A^a x_B^b}$$

Relation between K_p & K_c :

$$K_p = K_c \cdot (RT)^{\Delta n}$$

Relation between K_p & K_x :

$$K_p = K_x (P)^{\Delta n}$$
$$* \log \frac{K_2}{K_1} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]; \Delta H = \text{Enthalpy of reaction}$$

Relation between equilibrium constant & standard free energy change :

$$\Delta G^\circ = -2.303 RT \log K$$

Reaction Quotient (Q) :

$$\text{The values of expression } Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Degree of Dissociation (α) :

$\alpha = \text{no. of moles dissociated} / \text{initial no. of moles taken}$
 $= \text{fraction of moles dissociated out of 1 mole.}$

Note : % dissociation = $\alpha \times 100$

Observed molecular weight and Observed Vapour Density of the mixture :

Observed molecular weight of $A_n(g)$

$$\text{molecular weight of equilibrium mixture} \\ = \frac{\text{total no. of moles}}{\text{total no. of moles}}$$
$$\alpha = \frac{D - d}{(n-1) \times d} = \frac{M_T - M_0}{(n-1) M_0}$$

External factor affecting equilibrium :

Le Chatelier's Principle:

If a system at equilibrium is subjected to a disturbance or stress that changes any of the factors that determine the state of equilibrium, the system will react in such a way as to minimize the effect of the disturbance.

Effect of concentration :

- * If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction .
- * If the concentration of product is increased then equilibrium shifts in the backward direction

Effect of volume :

- * If volume is increased pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
- * If volume is increased then, for

$\Delta n > 0$ reaction will shift in the forward direction

$\Delta n < 0$ reaction will shift in the backward direction

$\Delta n = 0$ reaction will not shift.

Effect of pressure :

If pressure is increased at equilibrium then reaction will try to decrease the pressure, hence it will shift in the direction in which less no. of moles of gases are formed.

Effect of inert gas addition :

(i) Constant pressure :

If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

$\Delta n > 0$ reaction will shift in the forward direction

$\Delta n < 0$ reaction will shift in the backward direction

$\Delta n = 0$ reaction will not shift.

(ii) Constant volume :

Inert gas addition has no effect at constant volume.

Effect of Temperature :

Equilibrium constant is only dependent upon the temperature.

If plot of $\ln K$ vs $\frac{1}{T}$ is plotted then it is a straight line with slope $= - \frac{\Delta H^\circ}{R}$,
and intercept $= \frac{\Delta S^\circ}{R}$

- * For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature
- * For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature
- * For $\Delta H > 0$, reaction shifts in the forward direction with increase in temperature
- * For $\Delta H < 0$, reaction shifts in the backward direction with increases in temperature.
- * If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction .
- * If the concentration of product is increased then equilibrium shifts in the backward direction

Vapour Pressure of Liquid :

$$\text{Relative Humidity} = \frac{\text{Partial pressure of H}_2\text{O vapours}}{\text{Vapour pressure of H}_2\text{O at that temp.}}$$

Thermodynamics of Equilibrium :

$$\Delta G = \Delta G^\circ + 2.303 RT \log_{10} Q$$

$$\text{Vant Hoff equation- } \log \left(\frac{K_1}{K_2} \right) = \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

IONIC EQUILIBRIUM

OSTWALD DILUTION LAW :

- Dissociation constant of weak acid (K_a),

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If $\alpha \ll 1$, then $1 - \alpha \approx 1$ or $K_a = C\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times V}$

- Similarly for a weak base, $\alpha = \sqrt{\frac{K_b}{C}}$. Higher the value of K_a / K_b , strong is the acid / base.

Acidity and pH scale :

∴ $pH = -\log a_{H^+}$ (where a_{H^+} is the activity of H^+ ions = molar concentration for dilute solution).

[Note : pH can also be negative or > 14]

$$\begin{aligned} pH &= -\log [H^+]; & [H^+] &= 10^{-pH} \\ pOH &= -\log [OH^-]; & [OH^-] &= 10^{-pOH} \\ pK_a &= -\log K_a; & K_a &= 10^{-pK_a} \\ pK_b &= -\log K_b; & K_b &= 10^{-pK_b} \end{aligned}$$

PROPERTIES OF WATER :

1. In pure water $[H^+] = [OH^-]$ so it is Neutral.

2. Molar concentration / Molarity of water = 55.56 M.

3. Ionic product of water (K_w) :

$$K_w = [H^+][OH^-] = 10^{-14} \text{ at } 25^\circ C \text{ (experimentally)}$$

$$\begin{aligned} pH = 7 = pOH &\Rightarrow \text{neutral} \\ pH < 7 \text{ or } pOH > 7 &\Rightarrow \text{acidic} \\ pH > 7 \text{ or } pOH < 7 &\Rightarrow \text{Basic} \end{aligned}$$

4. Degree of dissociation of water :

$$\alpha = \frac{\text{no. of moles dissociated}}{\text{Total No. of moles initially taken}} = \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7}\%$$

5. Absolute dissociation constant of water :

$$K_a = K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

$$pK_a = pK_b = -\log (1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$$

$$K_a \times K_b = [H^+] [OH^-] = K_w$$

⇒ Note: for a conjugate acid-base pairs

$$pK_a + pK_b = pK_w = 14 \quad \text{at } 25\text{EC.}$$

$$pK_a \text{ of } H_3O^+ \text{ ions} = 1.74$$

$$pK_b \text{ of } OH^- \text{ ions} = 1.74.$$

○ pH Calculations of Different Types of Solutions:

(a) Strong acid solution :

(i) If concentration is greater than 10^{-6} M

In this case H^+ ions coming from water can be neglected,

(ii) If concentration is less than 10^{-6} M

In this case H^+ ions coming from water cannot be neglected

(b) Strong base solution :

Using similar method as in part (a) calculate first $[OH^-]$ and then use $[H^+] \times [OH^-] = 10^{-14}$

(c) pH of mixture of two strong acids :

Number of H^+ ions from I-solution = $N_1 V_1$

Number of H^+ ions from II-solution = $N_2 V_2$

$$[H^+] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

(d) pH of mixture of two strong bases :

$$[OH^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

(e) pH of mixture of a strong acid and a strong base :

If $N_1 V_1 > N_2 V_2$, then solution will be acidic in nature and

$$[H^+] = N = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$$

If $N_2 V_2 > N_1 V_1$, then solution will be basic in nature and

$$[OH^-] = N = \frac{N_2 V_2 - N_1 V_1}{V_1 + V_2}$$

(f) pH of a weak acid(monoprotic) solution :

$$K_a = \frac{[H^+] [OH^-]}{[HA]} = \frac{C \alpha^2}{1 - \alpha}$$

$$\text{if } \alpha \ll 1 \Rightarrow (1 - \alpha) \approx 1 \quad \Rightarrow \quad K_a \approx C \alpha^2$$

$$\Rightarrow \alpha = \sqrt{\frac{K_a}{C}} \quad (\text{is valid if } \alpha < 0.1 \text{ or } 10\%)$$

On increasing the dilution

$$\Rightarrow C \downarrow \Rightarrow \alpha \uparrow \quad \text{and } [H^+] \downarrow \Rightarrow pH \uparrow$$

RELATIVE STRENGTH OF TWO ACIDS :

$$\frac{[H^+] \text{ furnished by I acid}}{[H^+] \text{ furnished by II acid}} = \frac{c_1 \alpha_1}{c_2 \alpha_2} = \sqrt{\frac{k_{a_1} c_1}{k_{a_2} c_2}}$$

○ SALT HYDROLYSIS :

| Salt of | Type of hydrolysis | k_h | h | pH |
|-------------------------------|--------------------|-----------------------|------------------------------|---|
| (a) weak acid & strong base | anionic | $\frac{k_w}{k_a}$ | $\sqrt{\frac{k_w}{k_a c}}$ | $7 + \frac{1}{2} pK_a + \frac{1}{2} \log c$ |
| (b) strong acid & weak base | cationic | $\frac{k_w}{k_b}$ | $\sqrt{\frac{k_w}{k_b c}}$ | $7 - \frac{1}{2} pK_b - \frac{1}{2} \log c$ |
| (c) weak acid & weak base | both | $\frac{k_w}{k_a k_b}$ | $\sqrt{\frac{k_w}{k_a k_b}}$ | $7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$ |
| (d) Strong acid & strong base | ----- | do not hydrolyse | ----- | pH = 7 |

Hydrolysis of polyvalent anions or cations

For $[Na_3PO_4] = C$.

$$K_{a1} F K_{h3} = K_w$$

$$K_{a1} F K_{h2} = K_w$$

$$K_{a3} F K_{h1} = K_w$$

Generally pH is calculated only using the first step Hydrolysis

$$K_{h1} = \frac{Ch^2}{1-h} \approx Ch^2$$

$$h = \sqrt{\frac{K_{h1}}{C}} \Rightarrow [OH^-] = ch = \sqrt{K_{h1} \times C} \Rightarrow [H^+] = \sqrt{\frac{K_w \times K_{a3}}{C}}$$

$$\text{So } pH = \frac{1}{2} [pK_w + pK_{a3} + \log C]$$

BUFFER SOLUTION :

(a) **Acidic Buffer** : e.g. CH_3COOH and CH_3COONa . (weak acid and salt of its conjugate base).

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad [\text{Henderson's equation}]$$

(b) **Basic Buffer** : e.g. $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$. (weak base and salt of its conjugate acid).

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

SOLUBILITY PRODUCT :

$$K_{\text{sp}} = (x\text{s})^x (y\text{s})^y = x^x \cdot y^y \cdot (\text{s})^{x+y}$$

CONDITION FOR PRECIPITATION :

If ionic product $K_{\text{i,p}} > K_{\text{sp}}$ precipitation occurs,

if $K_{\text{i,p}} = K_{\text{sp}}$ saturated solution (precipitation just begins or is just prevented).

ELECTROCHEMISTRY

ELECTRODE POTENTIAL

For any electrode \rightarrow oxidation potential = – Reduction potential

$$E_{\text{cell}} = \text{R.P of cathode} - \text{R.P of anode}$$

$$E_{\text{cell}} = \text{R.P. of cathode} + \text{O.P of anode}$$

E_{cell} is always a +ve quantity & Anode will be electrode of low R.P

$$E E_{\text{cell}} = \text{SRP of cathode} - \text{SRP of anode}.$$

- **Greater the SRP value greater will be oxidising power.**

GIBBS FREE ENERGY CHANGE :

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

$$\Delta GE = -nFEE_{\text{cell}}$$

NERNST EQUATION : (Effect of concentration and temp on emf of cell)

$$\Delta G = \Delta GE + RT \ln Q \quad (\text{where } Q \text{ is reaction quotient})$$

$$\Delta GE = -RT \ln K_{\text{eq}}$$

$$E_{\text{cell}} = E E_{\text{cell}} - \frac{RT}{nF} \ln Q$$

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

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log Q \quad [\text{At } 298 \text{ K}]$$

At chemical equilibrium

$$\Delta G = 0 \quad ; \quad E_{\text{cell}} = 0.$$

○ $\log K_{\text{eq}} = \frac{nE^{\circ}_{\text{cell}}}{0.0591}.$

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{n} \log K_{\text{eq}}$$

For an electrode $M(s)/M^{n+}$.

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}.$$

CONCENTRATION CELL :

A cell in which both the electrodes are made up of same material.

For all concentration cell $E^{\circ}_{\text{cell}} = 0$.

(a) Electrolyte Concentration Cell :

eg. $Zn(s) / Zn^{2+}(c_1) \parallel Zn^{2+}(c_2) / Zn(s)$

$$E = \frac{0.0591}{2} \log \frac{C_2}{C_1}$$

(b) Electrode Concentration Cell :

eg. $Pt, H_2(P_1 \text{ atm}) / H^+(1M) \parallel H_2(P_2 \text{ atm}) / Pt$

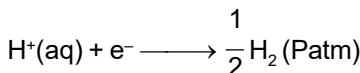
$$E = \frac{0.0591}{2} \log \left(\frac{P_1}{P_2} \right)$$

DIFFERENT TYPES OF ELECTRODES :

1. Metal-Metal ion Electrode $M(s)/M^{n+}$. $M^{n+} + ne^- \longrightarrow M(s)$

$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

2. Gas-ion Electrode $Pt / H_2(\text{Patm}) / H^+(XM)$
as a reduction electrode



$$E = E^{\circ} - 0.0591 \log \frac{P_{H_2}^{\frac{1}{2}}}{[H^+]}$$

3. Oxidation-reduction Electrode Pt / Fe²⁺, Fe³⁺
as a reduction electrode Fe³⁺ + e⁻ \longrightarrow Fe²⁺

$$E = E_E - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

4. Metal-Metal insoluble salt Electrode eg. Ag/AgCl, Cl⁻
as a reduction electrode AgCl(s) + e⁻ \longrightarrow Ag(s) + Cl⁻

$$E_{Cl^-/AgCl/Ag} = E_{Cl^-/AgCl/Ag}^0 - 0.0591 \log [Cl^-]$$

ELECTROLYSIS :

(a) K⁺, Ca⁺², Na⁺, Mg⁺², Al⁺³, Zn⁺², Fe⁺², H⁺, Cu⁺², Ag⁺, Au⁺³.

→
Increasing order of deposition.

(b) Similarly the anion which is stronger reducing agent (low value of SRP) is liberated first at the anode.

$$\begin{array}{c} SO^{2-} \\ | \\ 4 \end{array} \begin{array}{c} NO^- \\ | \\ 3 \end{array} \begin{array}{c} OH^- \\ | \\ 2 \end{array} \begin{array}{c} Cl^- \\ | \\ 1 \end{array} \begin{array}{c} Br^- \\ | \\ 0 \end{array} \begin{array}{c} I^- \\ | \\ -1 \end{array} \longrightarrow$$

Increasing order of deposition

FARADAY'S LAW OF ELECTROLYSIS :

First Law :

$$w = zq \quad w = Zit \quad Z = \text{Electrochemical equivalent of substance}$$

Second Law :

$$W \propto E \quad \frac{W}{E} = \text{constant} \quad \frac{W_1}{E_1} = \frac{W_2}{E_2} = \dots$$

$$\frac{W}{E} = \frac{i \times t \times \text{current efficiency factor}}{96500}.$$

$$\text{Current efficiency} = \frac{\text{actual mass deposited/produced}}{\text{Theoretical mass deposited/produced}} \times 100$$

CONDITION FOR SIMULTANEOUS DEPOSITION OF Cu & Fe AT CATHODE

$$E_E_{Cu^{2+}/Cu} - \frac{0.0591}{2} \log \frac{1}{Cu^{2+}} = E_E_{Fe^{2+}/Fe} - \frac{0.0591}{2} \log \frac{1}{Fe^{2+}}$$

Condition for the simultaneous deposition of Cu & Fe on cathode.

CONDUCTANCE :

$$\text{Conductance} = \frac{1}{\text{Resistance}}$$

☞ **Specific conductance or conductivity :**

$$\text{(Reciprocal of specific resistance)} \quad K = \frac{1}{\rho}$$

K = specific conductance

☞ **Equivalent conductance :**

$$\lambda_E = \frac{K \times 1000}{\text{Normality}} \quad \text{unit : } \text{-ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

☞ **Molar conductance :**

$$\lambda_m = \frac{K \times 1000}{\text{Molarity}} \quad \text{unit : } \text{-ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\text{specific conductance} = \text{conductance \%} \frac{\ell}{a}$$

KOHLRAUSCH'S LAW :

Variation of λ_{eq} / λ_M of a solution with concentration :

(i) Strong electrolyte

$$\lambda_M^c = \lambda_M^\infty - b \sqrt{c}$$

(ii) Weak electrolytes : $\lambda_\infty = n_+ \lambda_+^\infty + n_- \lambda_-^\infty$

where λ is the molar conductivity

n_+ = No of cations obtained after dissociation per formula unit

n_- = No of anions obtained after dissociation per formula unit

APPLICATION OF KOHLRAUSCH LAW :

1. Calculation of λ_M^0 of weak electrolytes :

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

2. To calculate degree of dissociation of a weak electrolyte

$$\alpha = \frac{\lambda_M^c}{\lambda_M^0} \quad ; \quad K_{eq} = \frac{c\alpha^2}{(1-\alpha)}$$

3. Solubility (S) of sparingly soluble salt & their K_{sp}

$$\lambda_M^c = \lambda_M^\infty = \kappa \% \frac{1000}{\text{solubility}}$$

$$K_{sp} = S^2.$$

Transport Number :

$$t_c = \left[\frac{\mu_c}{\mu_c + \mu_a} \right], \quad t_a = \left[\frac{\mu_a}{\mu_a + \mu_c} \right].$$

Where t_c = Transport Number of cation & t_a = Transport Number of anion

SOLUTION & COLLIGATIVE PROPERTIES

OSMOTIC PRESSURE :

(i) $\pi = \rho gh$ Where, ρ = density of soln., h = equilibrium height.
(ii) **Vant Hoff Formula** (For calculation of O.P.)

$$\pi = CST$$

$$\pi = CRT = \frac{n}{V} RT \text{ (just like ideal gas equation)}$$

$\therefore C$ = total conc. of all types of particles.

$$= C_1 + C_2 + C_3 + \dots$$

$$= \frac{(n_1 + n_2 + n_3 + \dots)}{V}$$

Note : If V_1 mL of C_1 conc. + V_2 mL of C_2 conc. are mixed.

$$\pi = \left(\frac{C_1 V_1 + C_2 V_2}{V_1 + V_2} \right) RT ; \quad \pi = \left(\frac{\pi_1 V_1 + \pi_2 V_2}{RT} \right)$$

Type of solutions :

(a) **Isotonic solution** \tilde{n} Two solutions having same O.P.

$$\pi_1 = \pi_2 \text{ (at same temp.)}$$

(b) **Hyper tonic** \tilde{n} If $\pi_1 > \pi_2 \Rightarrow$ 1st solution is hypertonic solution w.r.t. 2nd solution.

(c) **Hypotonic** \tilde{n} 2nd solution is hypotonic w.r.t. 1st solution.

Abnormal Colligative Properties : (In case of association or dissociation)

VANT HOFF CORRECTION FACTOR (i) :

$$i = \frac{\text{exp/observed / actual / abnormal value of colligative property}}{\text{Theoretical value of colligative property}}$$

$$= \frac{\text{exp./observed no. of particles / conc.}}{\text{Theoretical no. of particles}} = \frac{\text{observed molality}}{\text{Theoretical molality}}$$

$$= \frac{\text{theoretical molar mass(formula mass)}}{\text{experimental / observed molar mass(apparent molar mass)}}$$

○ $i > 1 \Rightarrow$ dissociation.

○ $i < 1 \Rightarrow$ association.

$$\text{○ } i = \frac{\pi_{\text{exp.}}}{\pi_{\text{theor}}}$$

$$\therefore \pi = iCRT$$

$$\pi = (i_1 C_1 + i_2 C_2 + i_3 C_3 + \dots) RT$$

Relation between i & α (degree of dissociation) :

$$i = 1 + (n - 1)\alpha \quad \text{Where, } n = x + y.$$

Relation b/w degree of association β & i .

$$i = 1 + \left(\frac{1}{n} - 1\right)\beta$$

RELATIVE LOWERING OF VAPOUR PRESSURE (RLVP) :

Vapour pressure : $P_{\text{Soln.}} < P$

$$\text{Lowering in VP} = P - P_s = \Delta P$$

$$\text{Relative lowering in vapour pressure} \quad \text{RLVP} = \frac{\Delta P}{P}$$

Raoult's law : (For non – volatile solutes)

Experimentally relative lowering in V.P = mole fraction of the non volatile solute in solutions.

$$\text{RLVP} = \frac{P - P_s}{P} = X_{\text{Solute}} = \frac{n}{n + N}$$

$$\frac{P - P_s}{P_s} = \frac{n}{N}$$

$$\frac{P - P_s}{P_s} = (\text{molality}) \% \frac{M}{1000}$$

(M = molar mass of solvent)

If solute gets associated or dissociated

$$\frac{P - P_s}{P_s} = \frac{i \cdot n}{N}$$

$$\frac{P - P_s}{P_s} = i \% (\text{molality}) \% \frac{M}{1000}$$

○ According to Raoult's law

(i) $p_1 = p_1^0 X_1$. where X_1 is the mole fraction of the solvent (liquid).

(ii) An alternate form $\rightarrow \frac{p_1^0 - p_1}{p_1^0} = X_2$.

Elevation in Boiling Point :

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

$$K_b = \frac{RT_b^2}{1000 \times L_{\text{vap}}} \quad \text{or} \quad K_b = \frac{RT_b^2 M}{1000 \times \Delta H_{\text{vap}}}$$

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

Depression in Freezing Point :

$$\therefore \Delta T_f = i \% K_f \cdot m.$$

$$K_f = \text{molal depression constant} = \frac{RT_f^2}{1000 \times L_{\text{fusion}}} = \frac{RT_f^2 M}{1000 \times \Delta H_{\text{fusion}}}.$$

Raoult's Law for Binary (Ideal) mixture of Volatile liquids :

$$P_A = X_A P_A^0 \quad \therefore \quad P_B = X_B P_B^0$$

if $P_A > P_B$ \therefore A is more volatile than B

\therefore B.P. of A < B.P. of B

\therefore According to Dalton's law

$$P_T = P_A + P_B = X_A P_A^0 + X_B P_B^0$$

x_A' = mole fraction of A in vapour above the liquid / solution.

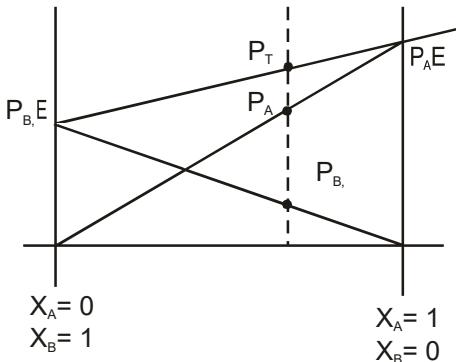
x_B' = mole fraction of B

$$P_A = X_A P_A^0 = X_A' P_T$$

$$P_B = X_B' P_T = X_B P_B^0$$

$$\frac{1}{P_T} = \frac{x_A'}{P_A E} + \frac{x_B'}{P_B E}$$

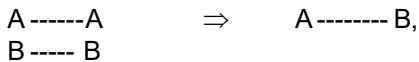
Graphical Representation :



A more volatile than B ($P_A E > P_B E$)

Ideal solutions (mixtures) :

Mixtures which follow Raoult's law at all temperature.



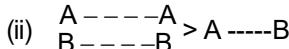
$$\begin{array}{ccc} \Delta H_{\text{mix}} = 0 & : & \Delta V_{\text{mix}} = 0 \\ \Delta S_{\text{mix}} = + \text{ve} \text{ as for process to proceed} & : & \Delta G_{\text{mix}} = - \text{ve} \end{array}$$

eg. (1) Benzene + Toluene.
(2) Hexane + heptane.
(3) $C_2H_5Br + C_2H_5I$.

Non-Ideal solutions : Which do not obey Raoult's law.

(a) Positive deviation : \tilde{n}

(i) $P_{T,\text{exp}} > (X_A P_A E_A + X_B P_B E_B)$



↓

Force of attraction

(iii) $\Delta H_{\text{mix}} = +\text{ve}$ energy absorbed

(iv) $\Delta V_{\text{mix}} = +\text{ve}$ ($1L + 1L > 2L$)

(v) $\Delta S_{\text{mix}} = +\text{ve}$

(vi) $\Delta G_{\text{mix}} = -\text{ve}$

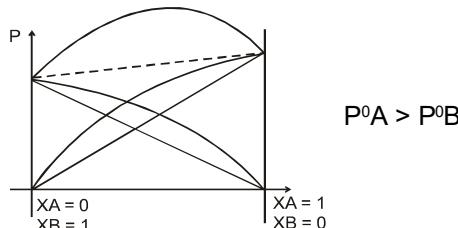
eg. $H_2O + CH_3OH$.

$H_2O + C_2H_5OH$

$C_2H_5OH + \text{hexane}$

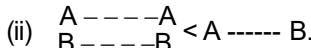
$C_2H_5OH + \text{cyclohexane}$.

$CHCl_3 + CCl_4 \rightarrow$ dipole dipole interaction becomes weak.



(b) Negative deviation

(i) $P_{T,\text{exp}} < X_A P_A E_A + X_B P_B E_B$

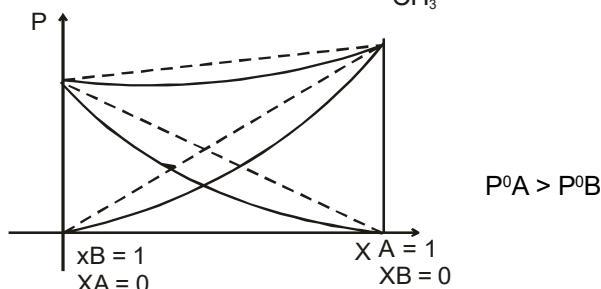
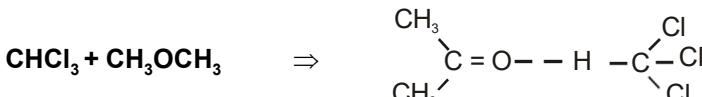
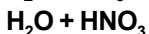


strength of force of attraction.

$$(iii) \Delta H_{\text{mix}} = -ve \quad (iv) \Delta V_{\text{mix}} = -ve \quad (1L + 1L < 2L)$$

$$(v) \Delta S_{\text{mix}} = +ve \quad (vi) \Delta G_{\text{mix}} = -ve$$

eg.



Immiscible Liquids :

$$(i) P_{\text{total}} = P_A + P_B$$

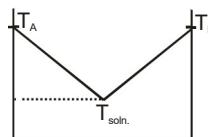
$$(ii) P_A = P_A^0 X_A = P_A^0 \quad [\text{Since, } X_A = 1].$$

$$(iii) P_B = P_B^0 X_B = P_B^0 \quad [\text{Since, } X_B = 1].$$

$$(iv) P_{\text{total}} = P_A^0 + P_B^0 \quad (v) \frac{P_A^0}{P_B^0} = \frac{n_A}{n_B}$$

$$(vi) \frac{P_A^0}{P_B^0} = \frac{W_A M_B}{M_A W_B}$$

$$P_A^0 = \frac{n_A RT}{V} ; \quad P_B^0 = \frac{n_B RT}{V}$$



B.P. of solution is less than the individual B.P.'s of both the liquids.

Henry Law :

This law deals with dissolution of gas in liquid i.e. mass of any gas dissolved in any solvent per unit volume is proportional to pressure of gas in equilibrium with liquid.

$$m \propto p$$

$$m = kp$$

weight of gas

$$m \rightarrow \frac{\text{weight of gas}}{\text{Volume of liquid}}$$

SOLID STATE

○ Classification of Crystal into Seven System

| Crystal System | Unit Cell Dimensions and Angles | Bravais Lattices | Example |
|----------------|---|----------------------------|-------------|
| Cubic | $a = b = c ; \alpha = \beta = \gamma = 90^\circ$ | SC, BCC, FCC | NaCl |
| Orthorhombic | $a \neq b \neq c ; \alpha = \beta = \gamma = 90^\circ$ | SC, BCC, end centred & FCC | S_R |
| Tetragonal | $a = b \neq c ; \alpha = \beta = \gamma = 90^\circ$ | SC, BCC | Sn, ZnO_2 |
| Monoclinic | $a \neq b \neq c ; \alpha = \gamma = 90^\circ \neq \beta$ | SC, end centred | S_M |
| Rhombohedral | $a = b = c ; \alpha = \beta = \gamma \neq 90^\circ$ | SC | Quartz |
| Triclinic | $a \neq b \neq c ; \alpha \neq \beta \neq \gamma \neq 90^\circ$ | SC | H_3BO_3 |
| Hexagonal | $a = b \neq c ; \alpha = \beta = 90^\circ ; \gamma = 120^\circ$ | SC | Graphite |

○ ANALYSIS OF CUBICAL SYSTEM

| | Property | SC | BCC | FCC |
|-------|------------------------------------|---------------|-----------------------|-----------------------|
| (i) | atomic radius (r) | $\frac{a}{2}$ | $\frac{\sqrt{3}}{4}a$ | $\frac{a}{2\sqrt{2}}$ |
| | $a =$ edge length | | | |
| (ii) | No. of atoms per unit cell (Z) | 1 | 2 | 4 |
| (iii) | C.No. | 6 | 8 | 12 |
| (iv) | Packing efficiency | 52% | 68% | 74% |
| (v) | No. voids | | | |
| | (a) octahedral (Z) | — | — | 4 |
| | (b) Tetrahedral ($2Z$) | — | — | 8 |

○ NEIGHBOUR HOOD OF A PARTICLE :

(I) Simple Cubic (SC) Structure :

| Type of neighbour | Distance | no. of neighbours |
|---------------------|-------------|------------------------|
| nearest | a | 6 (shared by 4 cubes) |
| (next) ¹ | $a\sqrt{2}$ | 12 (shared by 2 cubes) |
| (next) ² | $a\sqrt{3}$ | 8 (unshared) |

| | | | |
|------|--|-----------------------------|-------------------------|
| (II) | Body Centered Cubic (BCC) Structure : | | |
| | Type of neighbour | Distance | no.of neighbours |
| | nearest | $2r = a \frac{\sqrt{3}}{2}$ | 8 |
| | (next) ¹ | = a | 6 |
| | (next) ² | = $a\sqrt{2}$ | 12 |

| | | | |
|-------|--|-----------------------|--|
| (III) | Face Centered Cubic (FCC) Structure : | | |
| | Type of neighbour | Distance | no. of neighbours |
| | nearest | a | $12 = \left(\frac{3 \times 8}{2} \right)$ |
| | (next) ¹ | a | $6 = \left(\frac{3 \times 8}{4} \right)$ |
| | (next) ² | $a\sqrt{\frac{3}{2}}$ | 24 |

○ **DENSITY OF LATTICE MATTER (d) = $\frac{Z}{N_A} \left(\frac{M}{a^3} \right)$**

where N_A = Avogadro's No. M = atomic mass or molecular mass.

○ **IONIC CRYSTALS**

C.No. **Limiting radius ratio** $\left(\frac{r_+}{r_-} \right)$

- 3 0.155 – 0.225 (Triangular)
- 4 0.225 – 0.414 (Tetrahedral)
- 6 0.414 – 0.732 (Octahedral)
- 8 0.732 – 0.999 (Cubic).

○ **EXAMPLES OF A IONIC CRYSTAL**

(a) Rock Salt (NaCl) Coordination number (6 : 6)

(b) CsCl C.No. (8 : 8)

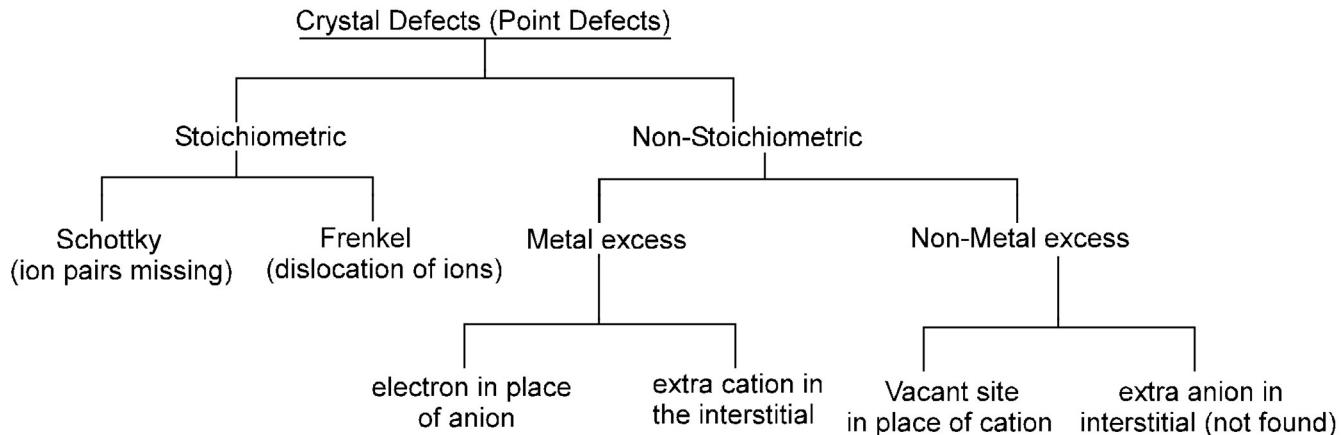
Edge length of unit cell :-

$$a_{sc} = \frac{2}{\sqrt{3}} (r_+ + r_-)$$

(c) Zinc Blende (ZnS) C.No. (4 : 4) $a_{fcc} = \frac{4}{\sqrt{3}} (r_{Zn^{2+}} + r_{S^{2-}})$

(d) Fluorite structure (CaF₂) C.No. (8 : 4) $a_{fcc} = \frac{4}{\sqrt{3}} (r_{Ca^{2+}} + r_{F^-})$

Crystal Defects (Imperfections)



CHEMICAL KINETICS & REDIOACTIVITY

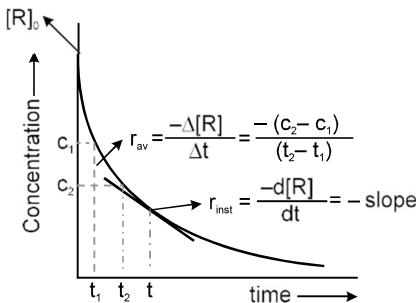
RATE/VELOCITY OF CHEMICAL REACTION :

$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{\text{mol / lit.}}{\text{sec}} = \text{mol lit}^{-1} \text{ time}^{-1} = \text{mol dm}^{-3} \text{ time}^{-1}$$

Types of Rates of chemical reaction :

For a reaction $R \longrightarrow P$

$$\text{Average rate} = \frac{\text{Total change in concentration}}{\text{Total time taken}}$$



$$R_{\text{instantaneous}} = \lim_{t \rightarrow 0} \left[\frac{\Delta c}{\Delta t} \right] = \frac{dc}{dt} = - \frac{d[R]}{dt} = \frac{d[P]}{dt}$$

RATE LAW (DEPENDENCE OF RATE ON CONCENTRATION OF REACTANTS) :

Rate = K (conc.)^{order} *is differential rate equation or rate expression*

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity

unit of K = (conc)^{1-order} time⁻¹

Order of reaction :



$R \propto [A]^p [B]^q$ Where p may or may not be equal to m_1 & similarly q may or may not be equal to m_2 .

p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and $(p + q)$ is **overall order of the reaction**.

INTEGRATED RATE LAWS :

C_0 or 'a' is initial concentration and C_t or $a - x$ is concentration at time 't'
 (a) **zero order reactions :**

Rate = k [conc.] $E = \text{constant}$

$$\text{Rate} = k = \frac{C_0 - C_t}{t} \quad \text{or} \quad C_t = C_0 - kt$$

Unit of K = mol lit⁻¹ sec⁻¹, Time for completion = $\frac{C_0}{k}$

$$\text{at } t_{1/2}, C_t = \frac{C_0}{2}, \text{ so } kt_{1/2} = \frac{C_0}{2} \Rightarrow t_{1/2} = \frac{C_0}{2k} \quad \therefore t_{1/2} \propto C_0$$

(b) First Order Reactions :

(i) Let a 1st order reaction is, $A \longrightarrow \text{Products}$

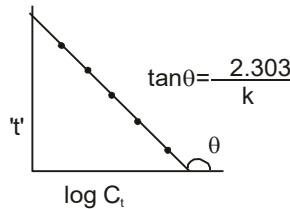
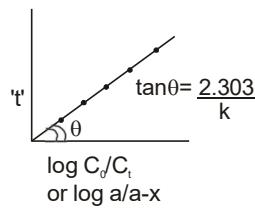
$$t = \frac{2.303}{k} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

$$\Rightarrow t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} = \text{Independent of initial concentration.}$$

$$t_{\text{Avg.}} = \frac{1}{k} = 1.44 t_{1/2}.$$

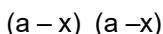
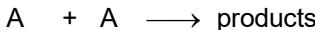
Graphical Representation :

$$t = -\frac{2.303}{k} \log C_t + \frac{2.303}{k} \log C_0$$



(c) Second order reaction :

2nd order Reactions
Two types



$$\therefore \frac{dx}{dt} = k (a-x)^2$$

$$\Rightarrow \frac{1}{(a-x)} - \frac{1}{a} = kt$$



$$\frac{dx}{dt} = k (a-x) (b-x)$$

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

METHODS TO DETERMINE ORDER OF A REACTION

(a) Initial rate method :

$$r = k [A]^a [B]^b [C]^c \quad \text{if} \quad [B] = \text{constant}$$
$$[C] = \text{constant}$$

then for two different initial concentrations of A we have

$$r_{01} = k [A_0]_1^a, \quad r_{02} = k [A_0]_2^a$$

$$\Rightarrow \frac{r_{01}}{r_{02}} = \left(\frac{[A_0]_1}{[A_0]_2} \right)^a$$

(b) Using integrated rate law : It is method of trial and error.

(c) Method of half lives :

$$\text{for } n^{\text{th}} \text{ order reaction} \quad t_{1/2} \propto \frac{1}{[R_0]^{n-1}}$$

(d) Ostwald Isolation Method :

$$\text{rate} = k [A]^a [B]^b [C]^c = k_0 [A]^a$$

METHODS TO MONITOR THE PROGRESS OF THE REACTION :

(a) *Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature or by measuring total volume of mixture under constant pressure and temperature.*

$$\therefore k = \frac{2.303}{t} \log \frac{P_0(n-1)}{nP_0 - P_t}$$

{Formula is not applicable when $n = 1$, the value of n can be fractional also.}

(b) *By titration method :*

$$1. \quad \therefore a \propto V_0 \quad a - x \propto V_t \quad \Rightarrow \quad k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

2. Study of acid hydrolysis of an ester.

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

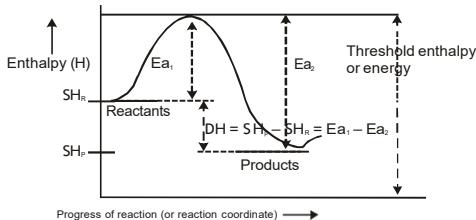
(c) *By measuring optical rotation produced by the reaction mixture :*

$$k = \frac{2.303}{t} \log \left(\frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty} \right)$$

EFFECT OF TEMPERATURE ON RATE OF REACTION.

$$T.C. = \frac{K_{t+10}}{K_t} \approx 2 \text{ to } 3 \text{ (for most of the reactions)}$$

Arhenius theory of reaction rate.



SH_r = Summation of enthalpies of reactants
 SH_p = Summation of enthalpies of products
 DH = Enthalpy change during the reaction
 Ea_1 = Energy of activation of the forward reaction
 Ea_2 = Energy of activation of the backward reaction

$$E_p > E_r \rightarrow \text{endothermic}$$

$$E_p < E_r \rightarrow \text{exothermic}$$

$$\Delta H = (E_p - E_r) = \text{enthalpy change}$$

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

$$E_{\text{threshold}} = E_{af} + E_r = E_b + E_p$$

Arhenius equation

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

$$r = k [\text{conc.}]^{\text{order}}$$

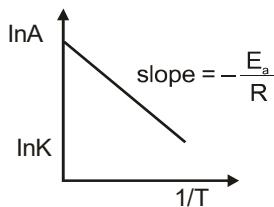
$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

$$\log k = \left(-\frac{E_a}{2.303 R} \right) \frac{1}{T} + \log A$$

If k_1 and k_2 be the rate constant of a reaction at two different temperature T_1 and T_2 respectively, then we have

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

❖ $\ln k = \ln A - \frac{E_a}{RT}$



$$E_a \geq 0$$

❖ $T \rightarrow \infty, K \rightarrow A.$

INORGANIC CHEMISTRY

PERIODIC TABLE & PERIODICITY

Development of Modern Periodic Table :

(a) **Dobereiner's Triads** : He arranged similar elements in the groups of three elements called as triads

(b) **Newland's Law of Octave** : He was the first to correlate the chemical properties of the elements with their atomic masses.

(c) **Luther Meyer's Classification** : He plotted a graph between atomic masses against their respective atomic volumes for a number of elements. He found the observations ; (i) elements with similar properties occupied similar positions on the curve, (ii) alkali metals having larger atomic volumes occupied the crests, (iii) transition elements occupied the troughs, (iv) the halogens occupied the ascending portions of the curve before the inert gases and
(v) alkaline earth metals occupied the positions at about the mid points of the descending portions of the curve. On the basis of these observations he concluded that the atomic volumes (a physical property) of the elements are the periodic functions of their atomic masses.

(d) Mendeleev's Periodic Table :

Mendeleev's Periodic Law

the physical and chemical properties of the elements are the periodic functions of their atomic masses.

| Periods | Number of Elements | Called as |
|-------------------------|--------------------|-------------------|
| (1) st n = 1 | 2 | Very short period |
| (2) nd n = 2 | 8 | Short period |
| (3) rd n = 3 | 8 | Short period |
| (4) th n = 4 | 18 | Long period |
| (5) th n = 5 | 18 | Long period |
| (6) th n = 6 | 32 | Very long period |
| (7) th n = 7 | 19 | Incomplete period |

Merits of Mendeleev's Periodic table:

- It has simplified and systematised the study of elements and their compounds.
- It has helped in predicting the discovery of new elements on the basis of the blank spaces given in its periodic table.

Demerits in Mendeleev's Periodic Table :

- Position of hydrogen is uncertain. It has been placed in IA and VIIA groups.
- No separate positions were given to isotopes.
- Anomalous positions of lanthanides and actinides in periodic table.
- Order of increasing atomic weights is not strictly followed in the arrangement of elements in the periodic table.
- Similar elements were placed in different groups.
- It didn't explain the cause of periodicity.

(e) Long form of the Periodic Table or Moseley's Periodic Table :

MODERN PERIODIC LAW (MOSELEY'S PERIODIC LAW) :

If the elements are arranged in order of their increasing atomic number, after a regular interval, elements with similar properties are repeated.

PERIODICITY :

The repetition of the properties of elements after regular intervals when the elements are arranged in the order of increasing atomic number is called periodicity.

CAUSE OF PERIODICITY :

The periodic repetition of the properties of the elements is due to the recurrence of similar valence shell electronic configurations after certain regular intervals.

The modern periodic table consists of horizontal rows (periods) and vertical columns (groups).

Periods :

There are seven periods numbered as 1, 2, 3, 4, 5, 6 and 7.

- Each period consists of a series of elements having same valence shell.
- Each period corresponds to a particular principal quantum number of the valence shell present in it.
- Each period starts with an alkali metal having outermost electronic configuration as ns^1 .
- Each period ends with a noble gas with outermost electronic configuration ns^2np^6 except helium having outermost electronic configuration as $1s^2$.
- Each period starts with the filling of new energy level.
- The number of elements in each period is twice the number of atomic orbitals available in energy level that is being filled.

Groups :

There are eighteen groups numbered as 1, 2, 3, 4, 5, 13, 14, 15, 16, 17, 18.

Group consists of a series of elements having similar valence shell electronic configuration.

CLASSIFICATION OF THE ELEMENTS :

(a) s-Block Elements

Group 1 & 2 elements constitute the s-block. General electronic configuration is [inert gas] ns^{1-2}
s-block elements lie on the extreme left of the periodic table.

(b) p-Block Elements

Group 13 to 18 elements constitute the p-block. General electronic configuration is [inert gas] $ns^2 np^{1-6}$

(c) d-Block Elements

Group 3 to 12 elements constitute the d-block. General electronic configuration is [inert gas] $(n-1)d^{1-10} ns^{1-2}$

(d) f-Block Elements

General electronic configuration is $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$. All f-block elements belong to 3rd group.

Elements of f-blocks have been classified into two series. (1) Ist inner transition or 4 f-series, contains 14 elements ₅₈Ce to ₇₁Lu. (2). IIInd inner transition or 5 f-series, contains 14 elements ₉₀Th to ₁₀₃Lr.

Prediction of period, group and block :

- Period of an element corresponds to the principal quantum number of the valence shell.
- The block of an element corresponds to the type of subshell which receives the last electron.
- The group is predicted from the number of electrons in the valence shell or/and penultimate shell as follows.
 - (a) For s-block elements ; Group no. = the no. of valence electrons
 - (b) For p-block elements ; Group no. = 10 + no. of valence electrons
 - (c) For d-block elements ; Group no. = no. of electrons in $(n-1)d$ sub shell + no. of electrons in valence shell.

Metals and nonmetals :

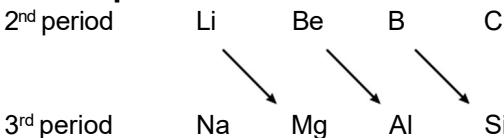
- ◆ The metals are characterised by their nature of readily giving up the electron(s) and from shinning lustre. Metals comprises more than 78% of all known elements and appear on the left hand side of the periodic table. Metals are usually solids at room temperature (except mercury, gallium). They have high melting and boiling points and are good conductors of heat and electricity. Oxides of metals are generally basic in nature (some metals in their higher oxidation state form acid oxides e.g. CrO_3).

- ◆ Nonmetals do not lose electrons but take up electrons to form corresponding anions. Nonmetals are located at the top right hand side of the periodic table. Nonmetals are usually solids, liquids or gases at room temperature with low melting and boiling points. They are poor conductors of heat and electricity. Oxides of nonmetals are generally acidic in nature.

Metalloids (Semi metals) :

The metalloids comprise of the elements B, Si, Ge, As, Sb and Te.

Diagonal relationship :



Diagonal relationship arises because of ;

- (i) on descending a group, the atoms and ions increase in size. On moving from left to right in the periodic table, the size decreases. Thus on moving diagonally, the size remains nearly the same. ($Li = 1.23 \text{ \AA}$ & $Mg = 1.36 \text{ \AA}$; $Li^+ = 0.76 \text{ \AA}$ & $Mg^{2+} = 0.72 \text{ \AA}$)
- (ii) it is sometimes suggested that the diagonal relationship arises because of diagonal similarity in electronegativity values. ($Li = 1.0$ & $Mg = 1.2$; $Be = 1.5$ & $Al = 1.5$; $B = 2.0$ & $Si = 1.8$)

The periodicity of atomic properties :

(i) Effective nuclear charge :

The effective nuclear charge (Z_{eff}) = $Z - \sigma$, (where Z is the actual nuclear charge (atomic number of the element) and σ is the shielding (screening) constant). The value of σ i.e. shielding effect can be determined using the Slater's rules.

(ii) Atomic radius :

(A) Covalent radius : It is one-half of the distance between the centres of two nuclei (of like atoms) bonded by a single covalent bond. Covalent radius is generally used for nonmetals.

(B) Vander Waal's radius (Collision radius) : It is one-half of the internuclear distance between two adjacent atoms in two nearest neighbouring molecules of the substance in solid state.

(C) Metallic radius (Crystal radius) :

It is one-half of the distance between the nuclei of two adjacent metal atoms in the metallic crystal lattice.

- ◆ Thus, the covalent, vander Wall's and metallic radius magnitude wise follows the order,

$$r_{\text{covalent}} < r_{\text{crystal}} < r_{\text{vander Walls}}$$

| Variation in a Period | Variation in a Group |
|--|--|
| In a period left to right : | In a group top to bottom : |
| Nuclear charge (Z) increases by one unit | Nuclear charge (Z) increases by more than one unit |
| Effective nuclear charge (Z_{eff}) also increases | Effective nuclear charge (Z_{eff}) almost remains constant because of increased screening effect of inner shells electrons. |
| But number of orbitals (n) remains constant | But number of orbitals (n) increases. |
| As a result, the electrons are pulled closer to the nucleus by the increased Z_{eff} . $r_n \propto \frac{1}{Z^2}$ Hence atomic radii decrease with increase in atomic number in a period from left to right. | The effect of increased number of atomic shells overweighs the effect of increased nuclear charge. As a result of this the size of atom increases from top to bottom in a given group. |

(iii) Ionic radius :

The effective distance from the centre of nucleus of the ion up to which it has an influence in the ionic bond is called ionic radius.

| Cation | Anion |
|---|--|
| <p>It is formed by the loss of one or more electrons from the valence shell of an atom of an element.</p> <p>Cations are smaller than the parent atoms because,</p> <p>(i) the whole of the outer shell of electrons is usually removed.</p> <p>(ii) in a cation, the number of positive charges on the nucleus is greater than number of orbital electrons leading to increased inward pull of remaining electrons causing contraction in size of the ion.</p> | <p>It is formed by the gain of one or more electrons in the valence shell of an atom of an element.</p> <p>Anions are larger than the parent atoms because</p> <p>(i) anion is formed by gain of one or more electrons in the neutral atom and thus number of electrons increases but magnitude of nuclear charge remains the same.</p> <p>(ii) nuclear charge per electrons is thus reduced and the electrons cloud is held less tightly by the nucleus leading to the expansion of the outer shell. Thus size of anion is increased.</p> |

(iv) Ionisation Energy :

Ionisation energy (IE) is defined as the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form a cation.



IE_1 , IE_2 & IE_3 are the Ist, Ind & IIIrd ionization energies to remove electron from a neutral atom, monovalent and divalent cations respectively. In general, $(IE)_1 < (IE)_2 < (IE)_3 < \dots$

◆ Factors Influencing Ionisation energy

(A) Size of the Atom : Ionisation energy decreases with increase in atomic size.

(B) Nuclear Charge : The ionisation energy increases with increase in the nuclear charge.

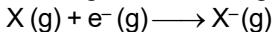
(C) **Shielding or screening effect** : The larger the number of electrons in the inner shells, greater is the screening effect and smaller the force of attraction and thus ionization energy (IE) decreases.

(D) **Penetration effect of the electron** : Penetration effect of the electrons follows the order s > p > d > f for, the same energy level. Higher the penetration of electron higher will be the ionisation energy.

(E) **Electronic Configuration** : If an atom has exactly half-filled or completely filled orbitals, then such an arrangement has extra stability.

(V) **Electron Gain Enthalpy : (CHANGED TOPIC NAME)**

The electron gain enthalpy $\Delta_{eg} H^\ominus$, is the change in standard molar enthalpy when a neutral gaseous atom gains an electron to form an anion.



The second electron gain enthalpy, the enthalpy change for the addition of a second electron to an initially neutral atom, invariably positive because the electron repulsion out weighs the nuclear attraction.

- Group 17 elements (halogens) have very high negative electron gain enthalpies (i.e. high electron affinity) because they can attain stable noble gas electronic configuration by picking up an electron.
- Across a period, with increase in atomic number, electron gain enthalpy becomes more negative
- As we move in a group from top to bottom, electron gain enthalpy becomes less negative
- Noble gases have large positive electron gain enthalpies
- Negative electron gain enthalpy of O or F is less than S or Cl.
- Electron gain enthalpies of alkaline earth metals are very less or positive
- Nitrogen has very low electron affinity
- (i) Electron affinity $\propto \frac{1}{\text{Atomic size}}$ (ii) Electron affinity \propto Effective nuclear charge (z_{eff})
(iii) Electron affinity $\propto \frac{1}{\text{Screening effect}}$. (iv) Stability of half filled and completely filled orbitals of a subshell is comparatively more and the addition of an extra electron to such a system is difficult and hence the electron affinity value decreases.

(VI) **Electronegativity :**

Electronegativity is a measure of the tendency of an element to attract shared electrons towards itself in a covalently bonded molecules.

(a) **Pauling's scale :**

$$\Delta = X_A - X_B = 0.208 \sqrt{E_{A-A} - \sqrt{E_{A-A} \times E_{B-B}}}$$

E_{A-B} = Bond enthalpy/ Bond energy of A – B bond.

E_{A-A} = Bond energy of A – A bond

E_{B-B} = Bond energy of B – B bond

(All bond energies are in kcal / mol)

$$\Delta = X_A - X_B = 0.1017 \sqrt{E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}}$$

All bond energies are in kJ / mol.

(b) Mulliken's scale :

$$\chi_M = \frac{IE + EA}{2}$$

Pauling's electronegativity χ_p is related to Mulliken's electronegativity χ_M as given below.

$$\chi_p = 1.35 (\chi_M)^{1/2} - 1.37$$

Mulliken's values were about 2.8 times larger than the Pauling's values.

(VII) Periodicity of Valence or Oxidation States :

There are many elements which exhibit variable valence. This is particularly characteristic of transition elements and actinoids.

(VIII) Periodic Trends and Chemical Reactivity :

- In a group, basic nature of oxides increases or acidic nature decreases. Oxides of the metals are generally basic and oxides of the nonmetals are acidic. The oxides of the metalloids are generally amphoteric in nature. The oxides of Be, Al, Zn, Sn, As, Pb and Sb are amphoteric.

- In a period the nature of the oxides varies from basic to acidic.



Strongly basic
Acidic



Basic
Strongly acidic



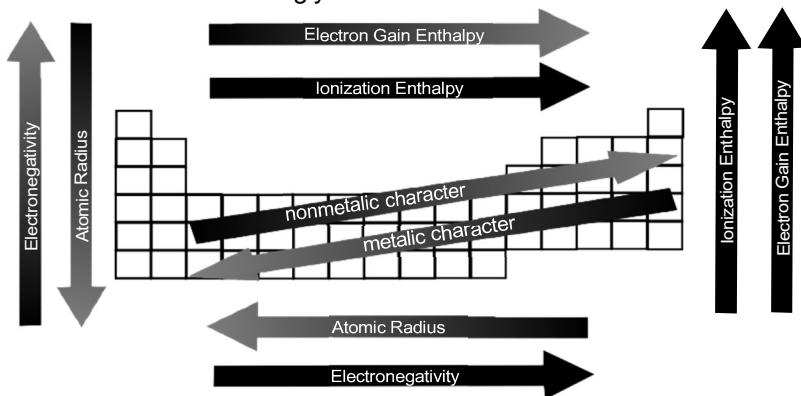
amphoteric



Weakly acidic



Acidic



CHEMICAL BONDING

Chemical Bond :

In the process each atom attains a stable outer electronic configuration of inert gases.

Ionic or Electrovalent Bond :

The formation of an ionic compound would primarily depends upon :

- * The ease of formation of the positive and negative ions from the respective neutral atoms.
- * The arrangement of the positive and negative ions in the solid, that is the lattice of the crystalline compound.

Conditions for the formation of ionic compounds :

- Electronegativity difference between two combining elements must be larger.
- Ionization enthalpy ($M(g) \rightarrow M^+(g) + e^-$) of electropositive element must be low.
- Negative value of electron gain enthalpy ($X(g) + e^- \rightarrow X^-(g)$) of electronegative element should be high.
- Lattice enthalpy ($M^+(g) + X^-(g) \rightarrow MX(s)$) of an ionic solid must be high.

Lattice Enthalpy :

The lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

Factors affecting lattice energy of an ionic compound :

- Lattice energy $\propto \frac{1}{r_+ + r_-}$ where $(r_+ + r_-) = \text{Inter-ionic Distance.}$
- Lattice energy $\propto Z_+, Z_-$

Z_+ \Rightarrow charge on cation in terms electronic charge.

Z_- \Rightarrow charge on anion in terms electronic charge.

Determination of lattice energy :

Born-Haber Cycle :

It inter relates the various energy terms involved during formation of an ionic compound.

It a thermochemical cycle based on the Hess's law of constant heat summation.

Hydration :

All the simple salts dissolve in water, producing ions, and consequently the solution conduct electricity. Since Li^+ is very small, it is heavily hydrated. This makes radius of hydrated Li^+ ion large and hence it moves only slowly. In contrast, Cs^+ is the least hydrated because of its bigger size and thus the radius of the Cs^+ ion is smaller than the radius of hydrated Li^+ , and hence hydrated Cs^+ moves faster, and conducts electricity more readily.

Hydrolysis :

Hydrolysis means reaction with water molecules ultimately leading to breaking of O-H bond into H^+ and OH^- ions.

Hydrolysis in covalent compounds takes place generally by two mechanisms

(a) By Coordinate bond formation : Generally in halides of atoms having vacant d-orbitals or of halides of atoms having vacant orbitals.

(b) By H-bond formation : For example in Nitrogen trihalides

General properties of ionic compounds :

- (a) **Physical state** : At room temperature ionic compounds exist either in solid state or in solution phase but not in gaseous state.
- (b) Simple ionic compounds do not show isomerism but isomorphism is their important characteristic.



- (c) **Electrical conductivity** :

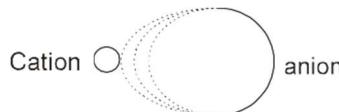
All ionic solids are good conductors in molten state as well as in their aqueous solutions because their ions are free to move.

- (d) **Solubility of ionic compounds** :

Soluble in polar solvents like water which have high dielectric constant

Covalent character in ionic compounds (Fajan's rule) :

Fajan's pointed out that greater is the polarization of anion in a molecule, more is covalent character in it.



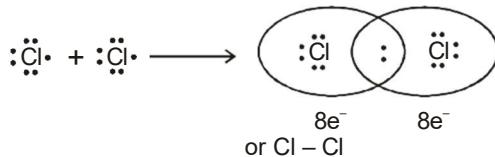
More distortion of anion, more will be polarisation then covalent character increases.

Fajan's gives some rules which govern the covalent character in the ionic compounds, which are as follows:

- (i) **Size of cation :** Size of cation \propto 1 / polarisation.
- (ii) **Size of anion :** Size of anion \propto polarisation
- (iii) **Charge on cation :** Charge on cation \propto polarisation.
- (iv) **Charge on anion :** Charge on anion \propto polarisation.
- (v) **Pseudo inert gas configuration of cation :**

Covalent Bond :

It forms by sharing of valence electrons between atoms to form molecules
e.g., formation of Cl_2 molecule :



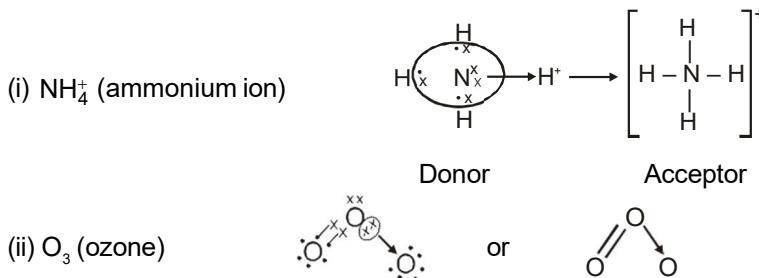
Covalent bond between two Cl atoms

The important conditions being that :

- (i) Each bond is formed as a result of sharing of an electron pair between the atoms.
- (ii) Each combining atom contributes at least one electron to the shared pair.
- (iii) The combining atoms attain the outer-shell noble gas configurations as a result of the sharing of electrons.

Coordinate Bond (Dative Bond):

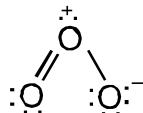
The bond formed between two atoms in which contribution of an electron pair is made by one of them while the sharing is done by both.



Other examples : H_2SO_4 , HNO_3 , H_3O^+ , N_2O , $[\text{Cu}(\text{NH}_3)_4]^{2+}$

Formal Charge :

$$\boxed{\text{Formal charge (F.C.)}} \quad \boxed{\text{On an atom in a Lewis structure}} = \boxed{\left[\text{Total number of valence electron in the free atom} \right] - \left[\text{Total number of non bonding (lone pair) electrons} \right] - \left(\frac{1}{2} \right) \left[\text{Total number of bonding (shared) electrons} \right]}$$



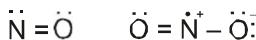
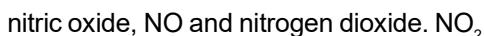
Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.

Limitations of the Octet Rule :

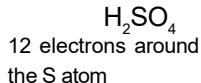
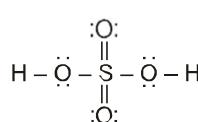
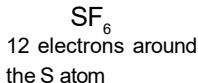
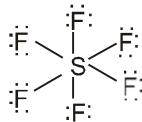
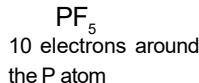
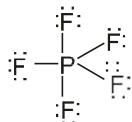
1. The incomplete octet of the central atom



2. Odd-electron molecules



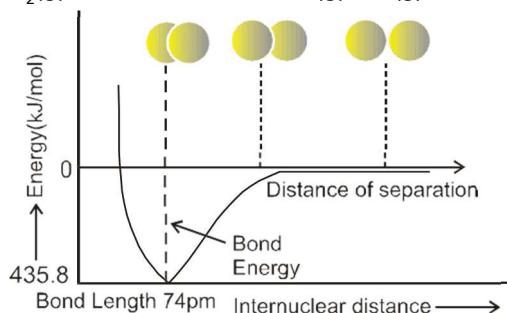
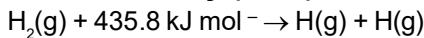
3. The expanded octet



4. Other drawbacks of the octet theory

- (i) some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2 , KrF_2 , XeOF_2 etc.,
- (ii) This theory does not account for the shape of molecules.
- (iii) It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

Valence bond theory (VBT) :



Orbital Overlap Concept

according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present, in the valence shell having opposite spins.

Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into two types depending upon the types of overlapping :

- (i) sigma (σ) bond, and (ii) pi (π) bond

(i) **Sigma (σ) bond :** This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis.

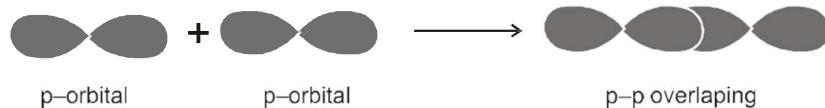
- s-s overlapping



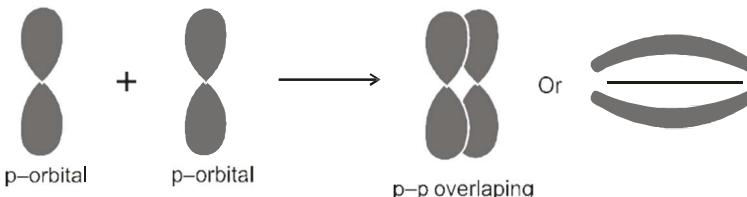
- s-p overlapping:



- p-p overlapping : This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



(ii) **$\pi(\pi)$ bond** : In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis.



Strength of Sigma and pi Bonds :

In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent.

Valence shell electron pair repulsion (VSEPR) theory :

The main postulates of VSEPR theory are as follows:

- (i) The shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded] around the central atom.
- (ii) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- (iii) These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- (iv) The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- (v) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- (vi) Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decreases in the order : lone pair (ℓp) - lone pair (ℓp) $>$ lone pair (ℓp) - bond pair (bp) $>$ bond pair (bp) - bond pair (bp)

Hybridisation :

Salient features of hybridisation :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation :

- (i) The orbitals present in the valence shell of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is the orbital that undergo hybridization and not the electrons.

Determination of hybridisation of an atom in a molecule or ion:

Steric number rule (given by Gillespie) :

Steric No. of an atom = number of atom bonded with that atom + number of lone pair(s) left on that atom.

Table-3

| Steric Number | Types of Hybridisation | Geometry |
|---------------|--------------------------------|------------------------|
| 2 | sp | Linear |
| 3 | sp ² | Trigonal planar |
| 4 | sp ³ | Tetrahedral |
| 5 | sp ³ d | Trigonal bipyramidal |
| 6 | sp ³ d ² | Octahedral |
| 7 | sp ³ d ³ | Pentagonal bipyramidal |

Hybridization Involving d-orbital :

Type of 'd' orbital involved

| | |
|--------------------------------|---|
| sp ³ d | d _{Z²} |
| sp ³ d ² | d _{x²-y²} & d _{Z²} |
| sp ³ d ³ | d _{x²-y²} , d _{Z²} & d _{xy} |
| dsp ² | d _{x²-y²} |

Molecular Orbital Theory (MOT) :

developed by F. Hund and R.S. Mulliken in 1932.

- (i) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.
- (ii) 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.**
- (iii) 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.
- (iv) The molecular orbitals like the atomic orbitals are filled in accordance with the **Aufbau principle** obeying the **Pauli Exclusion principle** and the **Hund's Rule of Maximum Multiplicity**. But the filling order of these molecular orbitals is always **experimentally decided**, there is no rule like (n + l) rule in case of atomic orbitals.

Conditions for the combination of 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 for molecular orbitals :

The increasing order of energies of various molecular orbitals for O₂ and F₂ is given below :

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

The important characteristic feature of this order is that the **energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.**

Bond Order

Bond order (b.o.) = C (N_b - N_a)

A positive bond order (i.e., N_b > N_a) means a stable molecule while a negative (i.e., N_b < N_a) or zero (i.e., N_b = N_a) bond order means an unstable molecule.

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 :

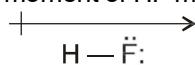
If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field) e.g., N₂ molecule.

Dipole moment :

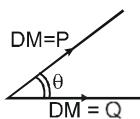
Dipole moment (μ) = Magnitude of charge (q) \times distance of separation (d)
Dipole moment is usually expressed in Debye units (D). The conversion factors are

- 1 D = 3.33564 Q 10⁻³⁰ Cm, where C is coulomb and m is meter.
- 1 Debye = 1 Q 10⁻¹⁸ e.s.u. cm.

For example the dipole moment of HF may be represented as



The shift in electron density is represented by crossed arrow ($\uparrow \longrightarrow$) above the Lewis structure to indicate the direction of the shift. A molecule will have a dipole moment if the summation of all of the individual moment vector is non-zero.



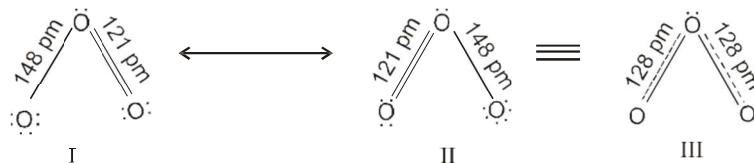
$$R = \sqrt{P^2 + Q^2 + 2PQ \cos \theta},$$

where R is resultant dipole moment.

Resonance :

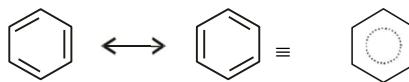
Definition : Resonance may be defined as the phenomenon in which two or more structures involving identical position of atom, can be written for a particular compound.

For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below :



Resonance in the O_3 molecule

Resonance Hybrid : It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of maximum covalence for the atoms.



Resonance hybrid

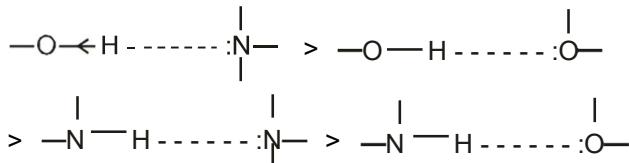
Hydrogen Bond :



Conditions required for H-bond :

- Molecule should have more electronegative atom (F, O, N) linked to H-atom.
- Size of electronegative atom should be smaller.
- A lone pair should be present on electronegative atom.

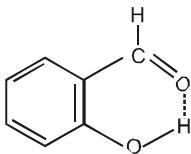
○ Order of H-bond strength



TYPES OF H-BONDS :

(A) **Intramolecular H-Bonding :**

it is formed when hydrogen atom is present in between the two highly electronegative (F, O, N) atoms within the same molecule.



o-hydroxy benzaldehyde

It has lower boiling point (i.e. more volatile) than its para-derivative

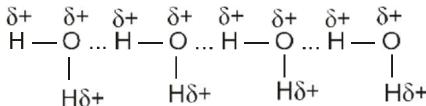
Necessary conditions for the formation of intramolecular hydrogen-bonding:

- the ring formed as a result of hydrogen bonding should be planar.
- a 5- or 6- membered ring should be formed.
- interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

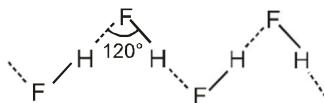
(B) **Intermolecular H-Bonding :**

it is formed between two different molecules of the same or different compounds.

(a) **In water molecules**



(b) The hydrogen bonds in HF link the F atom of one molecule with the H-atom of another molecule, thus forming a zig-zag chain $(\text{HF})_n$ in both the solid and also in the liquid.



Intermolecular forces (Vander Waalís Forces) :

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of following types.

Metallic bond :

Two models are considered to explain metallic bonding:

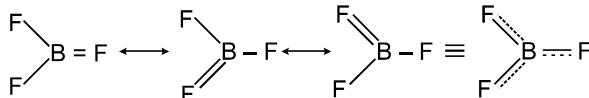
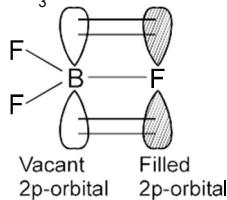
> Electron-sea model (B) Band model

Some special bonding situations :

(a) Electron deficient bonding: There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds. These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds (3c-2e) present in diborane B_2H_6 , $Al_2(CH_3)_6$, $BeH_2(s)$ and bridging metal carbonyls.

(b) Back Bonding : Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair(generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length.

For example, in BF_3 ,



the extent of back bonding in boron trihalides.



COORDINATION COMPOUNDS

ADDITION COMPOUNDS :

They are formed by the combination of two or more stable compounds in stoichiometric ratio. These are

- (1) Double salts and (2) Coordination compounds

DOUBLE SALTS :

Those addition compounds which lose their identity in solutions

e.g. K_2SO_4 , $Al_2(SO_4)_3$

COORDINATION COMPOUNDS :

Those addition compounds which retain their identity (i.e. doesn't lose their identity) in solution are



Central Atom/Ion :

In a coordination entity—the atom/ion to which are bound a fixed number of ligands in a definite geometrical arrangement around it.

Ligands :

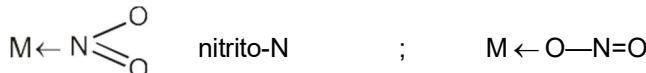
The neutral molecules, anions or cations which are directly linked with central metal atom or ion in the coordination entity are called ligands.

Chelate ligand :

Chelate ligand is a di or polydentate ligand which uses its two or more donor atoms to bind a single metal ion producing a ring.

Ambidentate Ligand :

Ligands which can ligate through two different atoms present in it



nitrito-O

$M \leftarrow SCN$ thiocyanato or thiocyanato-S ;

$M \leftarrow NCS$ isothiocyanato or thiocyanato-N

Coordination Number :

The number of ligand donor atoms to which the metal is directly attached.

Oxidation number of Central Atom :

The oxidation number of the central atom is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. $[Fe(CN)_6]^{3-}$ is +3 and it is written as Fe(III).

DENTICITY AND CHELATION :

Table : 1

Common Monodentate Ligands

| Common Name | IUPAC Name | Formula |
|-------------------------|---|---|
| methyl isocyanide | methylisocyanide | CH ₃ NC |
| triphenyl phosphine | triphenyl phosphine/triphenyl phosphane | PPPh ₃ |
| pyridine | pyridine | C ₅ H ₅ N (py) |
| ammonia | ammine | NH ₃ |
| methyl amine | methylamine | MeNH ₂ |
| water | aqua or aquo | H ₂ O |
| carbonyl | carbonyl | CO |
| thiocarbonyl | thiocarbonyl | CS |
| nitrosyl | nitrosyl | NO |
| fluoro | fluoro or fluorido* | F ⁻ |
| chloro | chloro or chlorido* | Cl ⁻ |
| bromo | bromo or bromido* | Br ⁻ |
| iodo | iodo or iodido* | I ⁻ |
| cyano | cyanido or cyanido-C* (C-bonded) | CN ⁻ |
| isocyano | isocyanido or cyanido-N* (N-bonded) | NC ⁻ |
| thiocyanato | thiocyanato-S(S-bonded) | SCN ⁻ |
| isothiocyanato | thiocyanato-N(N-bonded) | NCS ⁻ |
| cyanato (cyanate) | cyanato-O (O-bonded) | OCN ⁻ |
| isocyanato (isocyanate) | cyanato-N (N-bonded) | NCO ⁻ |
| hydroxo | hydroxo or hydroxido* | OH ⁻ |
| nitro | nitrito-N (N-bonded) | NO ₂ ⁻ |
| nitrito | nitrito-O (O-bonded) | ONO ⁻ |
| nitrate | nitrate | NO ₃ ⁻ |
| amido | amido | NH ₂ ⁻ |
| imido | imido | NH ²⁻ |
| nitride | nitrido | N ³⁻ |
| azido | azido | N ₃ ⁻ |
| hydride | hydrido | H ⁻ |
| oxide | oxido | O ²⁻ |
| peroxide | peroxido | O ₂ ²⁻ |
| superoxide | superoxido | O ₂ ⁻ |
| acetate | acetato | CH ₃ COO ⁻ |
| sulphate | sulphato | SO ₄ ²⁻ |
| thiosulphate | thiosulphato | S ₂ O ₃ ²⁻ |
| sulphite | sulphito | SO ₃ ²⁻ |
| hydrogen sulphite | hydrogensulphito | HSO ₃ ⁻ |
| sulphide | sulphido or thio | S ²⁻ |
| hydrogen sulphide | hydrogensulphido or mercapto | HS ⁻ |
| thionitrito | thionitrito | (NOS) ⁻ |
| nitrosylium | nitrosylium or nitrosonium | NO ⁺ |
| nitronium | nitronium | NO ₂ ⁺ |

* The 2004 IUPAC draft recommends that anionic ligands will end with-ido.

Table : 2
Common Chelating Amines

| Chelating Points | Common Name | IUPAC Name | Abbreviation | Formula |
|------------------|-----------------------------|---|--------------|--|
| bidentate | ethylenediamine | 1,2-ethanediamine/ethane-1,2-diamine | en | $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ |
| bidentate | propanediamine | 1,2-propanediamine | pn | $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$ |
| tridentate | diethylenetriamine | [N-(2-aminoethyl)-1,2-ethanediamine or diethylenetriamine | dien | $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ |
| tetradentate | triethylenetetraamine | [N, N'-bis-(2-aminoethyl)-1,2-ethanediamine or triethylenetetraamine | trien | $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ |
| | triaminotriethylamine | β, β', β'' -tris(2-aminoethyl) amine. | | |
| pentadentate | tetraethylenepentaamine | 1,4,7,10-pentaazatridecane or tetraethylenepentaamine | | $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ |
| hexadentate | ethylenediaminetetraacetate | 1,2-ethanediyil (dinitrilo) tetraacetate or ethylenediaminetetraacetate | EDTA | |

Table : 3
Common Multidentate (Chelating) Ligands

| Common Name | IUPAC Name | Abbreviation | Formula | Structure |
|-----------------------------|---|--------------|---|-----------|
| acetylacetato | 2,4-pentanediono or acetylacetato | acac | $\text{CH}_3\text{COCHCOCH}_3^-$ | |
| 2,2'-bipyridine | 2,2'-bipyridyl | bipy | $\text{C}_{10}\text{H}_8\text{N}_2$ | |
| oxalato | oxalato | ox | $\text{C}_2\text{O}_4^{2-}$ | |
| dimethylglyoximato | butanedienedioxime or dimethylglyoximato | DMG | $\text{HONC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{NO}^-$ | |
| ethylenediaminetetraacetato | 1,2-ethanediyil (dinitrilo) tetraacetato or ethylenediaminetetraacetato | EDTA | $(\text{HOOCCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2$ | |

Homoleptic and heteroleptic complexes

Complexes in which a metal is bound to only one type of donor groups, e.g., $[\text{Cr}(\text{NH}_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one type of donor groups, e.g., $[\text{Co}(\text{NH}_3)_3\text{H}_2\text{O}_2\text{Br}]^+$, are known as heteroleptic.

Nomenclature of Coordination Compounds

Writing the formulas of Mononuclear Coordination Entities :

- (i) The central atom is placed first.
- (ii) The ligands are then placed in alphabetical order. The placement of a ligand in the list does not depend on its charge.
- (iii) Polydentate ligands are also placed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.
- (iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligands abbreviations are also enclosed in parentheses.
- (v) There should be no space between the ligands and the metal within a coordination sphere.
- (vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$ etc.
- (vii) The charge of the cation(s) is balanced by the charge of the anion(s).

Writing the name of Mononuclear Coordination Compounds :

- (i) Like simple salts the cation is named first in both positively and negatively charged coordination entities.
- (ii) The ligands are named in an alphabetical order (according to the name of ligand, not the prefix) before the name of the central atom/ion.
- (iii) Names of the anionic ligands end in -o and those of neutral ligands are the same except aqua for H_2O , ammine for NH_3 , carbonyl for CO , thiocarbonyl for CS and nitrosyl for NO . But names of cationic ligands end in -ium.
- (iv) Prefixes mono, di, tri, etc., are used to indicate the number of the one kind of ligands in the coordination entity. When the names of the ligands include a numerical prefix or are complicated or whenever the use of normal prefixes creates some confusion, it is set off in parentheses and the second set of prefixes is used.

| | | |
|---|-------|----------|
| 2 | di | bis |
| 3 | tri | tris |
| 4 | tetra | tetrakis |
| 5 | penta | pentakis |
| 6 | hexa | hexakis |
| 7 | hepta | heptakis |

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in the parentheses after the name of metal.

(vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix - ate. For example, Co in a complex anion, $[\text{Co}(\text{SCN})_4]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions.

| | | | |
|-------------|-----------|-----------|----------|
| iron (Fe) | ferrate | lead (Pb) | plumbate |
| silver (Ag) | argentate | tin (Sn) | stannate |
| gold (Au) | aurate | | |

(vii) The neutral complex molecule is named similar to that of the complex cation.

Werner's Theory :

According to Werner most elements exhibit two types of valencies :

(a) Primary valency and (b) Secondary valency.

(a) Primary valency :

This corresponds to oxidation state of the metal ion. This is also called principal, ionisable or ionic valency. It is satisfied by negative ions and its attachment with the central metal ion is shown by dotted lines.

(b) Secondary or auxiliary valency :

It is also termed as coordination number (usually abbreviated as CN) of the central metal ion. It is non-ionic or non-ionisable (i.e. coordinate covalent bond type). In the modern terminology, such spatial arrangements are called coordination polyhedra and various possibilities are

| | | | |
|----------|------------------------------|----------|-------------|
| C.N. = 2 | linear | C.N. = 3 | Triangular |
| C.N. = 4 | tetrahedral or square planar | C.N. = 6 | octahedral. |

Effective Atomic Number Rule given by Sidgwick :

Effective Atomic Number (EAN) = Atomic no. of central metal – Oxidation state of central metal + No. of electrons donated by ligands.

Valence Bond Theory :

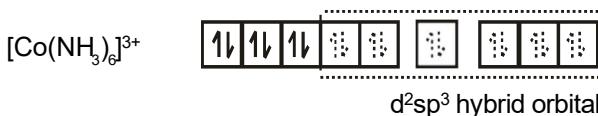
The model utilizes hybridisation of $(n-1)$ d, ns, np or ns, np, nd orbitals of metal atom or ion to yield a set of equivalent orbitals of definite geometry to account for the observed structures such as octahedral, square planar and tetrahedral, and magnetic properties of complexes. The number of unpaired electrons, measured by the magnetic moment of the compounds determines which d-orbitals are used.

TABLE :

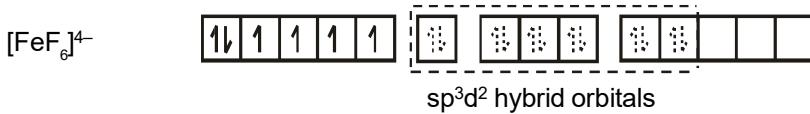
| Coordiantion number of metal | Type of hybridisation | Shape of complex |
|------------------------------|--------------------------------|----------------------|
| 4 | sp ³ | Tetrahedral |
| 4 | dsp ² | Square planer |
| 5 | sp ³ d | Trigonal bipyramidal |
| 6 | sp ³ d ² | Octahedral |
| 6 | d ² sp ³ | Octahedral |

Coordination Number Six :

In the diamagnetic octahedral complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration represented as shown below.

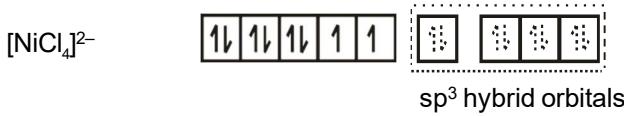


The complex $[\text{FeF}_6]^{4-}$ is paramagnetic and uses outer orbital (4d) in hybridisation (sp³d²) ; it is thus called as outer orbital or high spin or spin free complex. So,

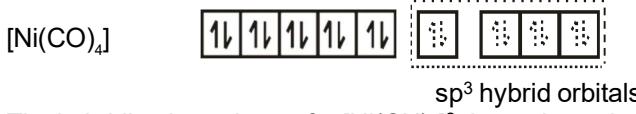


Coordination Number Four :

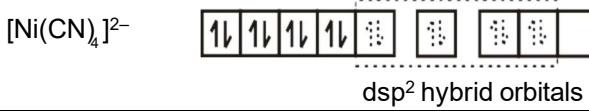
In the paramagnetic and tetrahedral complex $[\text{NiCl}_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration 3d⁸. The hybridisation scheme is as shown in figure.



Similarly complex $[\text{Ni}(\text{CO})_4]$ has tetrahedral geometry and is diamagnetic as it contains no unpaired electrons. The hybridisation scheme is as shown in figure.



The hybridisation scheme for $[\text{Ni}(\text{CN})_4]^{2-}$ is as shown in figure.



It suffers from the following shortcomings :

1. A number of assumptions are involved.
2. There is no quantitative interpretation of magnetic data.
3. It has nothing to say about the spectral (colour) properties of coordination compounds.
4. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
5. It does not make exact predictions regarding the tetrahedral and square-planar structures of 4-coordinate complexes.
6. It does not distinguish between strong and weak ligands.

Magnetic Properties of Coordination Compounds :

$$\text{Magnetic Moment} = \sqrt{n(n+2)} \text{ Bohr Magnetons};$$

$$n = \text{number of unpaired electrons}$$

For metal ions with upto three electrons in the d-orbitals like Ti^{3+} , (d^1); V^{3+} (d^2); Cr^{3+} (d^3); two vacant d-orbitals are easily available for octahedral hybridisation. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three 3d electrons are present, like in Cr^{2+} and Mn^{3+} (d^4); Mn^{2+} and Fe^{3+} (d^5); Fe^{2+} and Co^{3+} (d^6); the required two vacant orbitals for hybridisation is not directly available (as a consequence of Hund's rules). Thus, for d^4 , d^5 and d^6 cases, two vacant d-orbitals are only available for hybridisation as a result of pairing of 3d electrons which leaves two, one and zero unpaired electrons respectively.

Crystal Field Theory :

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand.

(a) Crystal field splitting in octahedral coordination entities :

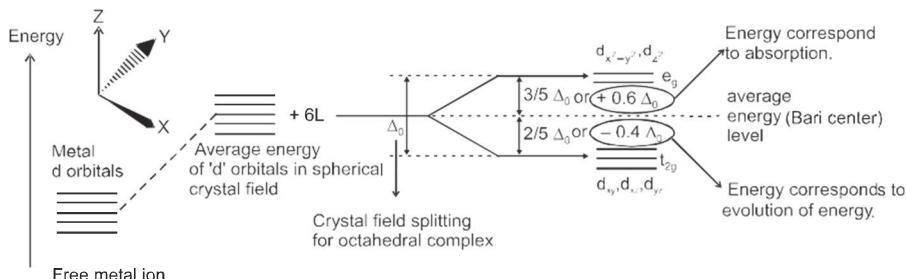
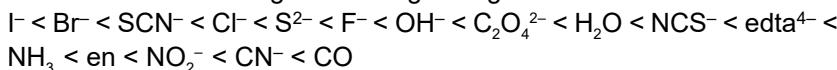


Figure showing crystal field splitting in octahedral complex.

The crystal field splitting, Δ_0 , depends upon the fields produced by the ligand and charge on the metal ion. Ligands can be arranged in a series in the orders of increasing field strength as given below :



Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands.

Calculation of Crystal Field stabilisation energy (CFSE)

$$\text{Formula : CFSE} = [-0.4(n)t_{2g} + 0.6(n')e_g]\Delta_0 + *n\text{P}.$$

where n & n' are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex. $*n$ represents the number of extra electron pairs formed because of the ligands in comparison to normal degenerate configuration.

(b) Crystal field splitting in tetrahedral coordination entities :

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that

$$\Delta_t = (4/9)\Delta_0.$$

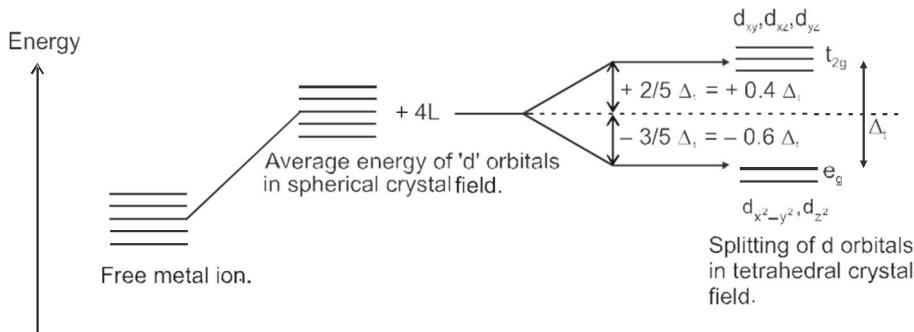


Figure showing crystal field splitting in tetrahedral complex.

Colour in Coordination Compounds :

According to the crystal field theory the colour is due to the d-d transition of electron under the influence of ligands. We know that the colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmission or reflection of the rest of the wavelengths.

Limitations of crystal field theory

- (1) It considers only the metal ion d-orbitals and gives no consideration at all to other metal orbitals (such as s, p_x, p_y and p_z orbitals).
- (2) It is unable to account satisfactorily for the relative strengths of ligands. For example it gives no explanation as to why H₂O is a stronger ligand than OH⁻ in the spectrochemical series.
- (3) According to this theory, the bond between the metal and ligands are purely ionic. It gives no account on the partly covalent nature of the metal ligand bonds.
- (4) The CFT cannot account for the π -bonding in complexes.

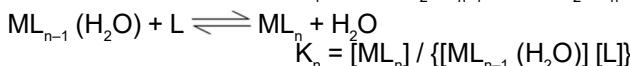
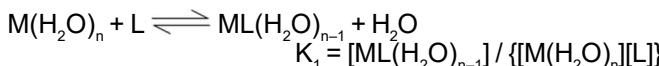
Stability of Coordination Compounds :

The stability of a coordination compound [ML_n] is measured in terms of the stability constant (equilibrium constant) given by the expression,

$$\beta_n = [ML_n]/[M(H_2O)_n][L]^n$$

for the overall reaction : $M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$

By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant, K₁, K₂, K₃, K_n for each step as represented below :



$$\beta_n = K_1 \times K_2 \times K_3 \times \dots \times K_n$$

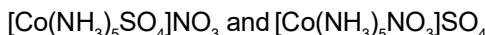
β_n , the stability constant, is related to thermodynamic stability when the system has reached equilibrium.

ISOMERISM :

(1) Structural isomerism :

(A) Ionisation isomerism :

This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligand and can displace a ligand which can then become the counter ion.



(B) Solvate / hydrate isomerism :

It occurs when water forms a part of the coordination entity or is outside it.

| Complex | Reaction with AgNO ₃ | Reaction with conc. H ₂ SO ₄ (dehydrating agent) |
|--|---------------------------------|--|
| [Cr(H ₂ O) ₆]Cl ₃ | in the molar ratio of 3:1 | No water molecule is lost or no reaction |
| [CrCl(H ₂ O) ₅]Cl ₂ .H ₂ O | in the molar ratio of 2:1 | one mole of water is lost per mole of complex |
| [CrCl ₂ (H ₂ O) ₄]Cl ₂ .2H ₂ O | in the molar ratio of 1:1 | two mole of water are lost per mole of complex |

(C) Linkage isomerism :
 In some ligands, like ambidentate ligands, there are two possible coordination sites. In such cases, linkage isomerism exist. e.g.,
For example : $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$ & $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$.

(D) Coordination isomerism :
 Coordination compounds made up of cationic and anionic coordination entities show this type of isomerism due to the interchange of ligands between the cation and anion entities. Some of the examples are : $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6](\text{Co}(\text{CN})_6)$

(E) Ligand isomerism :
 Since many ligands are organic compounds which have possibilities for isomerism, the resulting complexes can show isomerism from this source.

(F) Polymerisation isomerism :
 Considered to be a special case of coordination isomerism, in this the various isomers differ in formula weight from one another, so not true isomers in real sense.

(2). Stereoisomerism

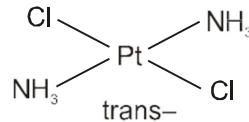
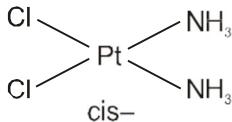
Geometrical Isomerism

Geometrical isomerism is common among coordination compounds with coordination numbers 4 and 6.

Coordination Number Four :

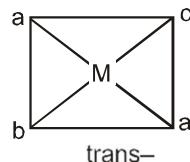
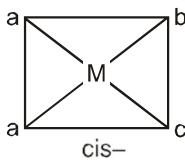
Tetrahedral Complex : The tetrahedral compounds can not show geometrical isomerism as we all know that all four positions are equivalent in tetrahedral geometry.

Square Planar Complex :

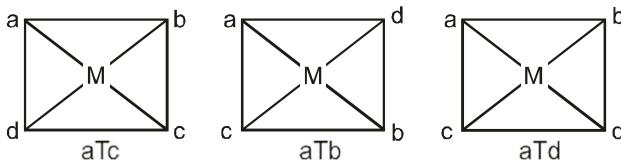


Geometrical isomers (cis and trans) of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.

Square planar complex of the type Ma_2bc (where a,b,c are unidentates) shows two geometrical isomers.

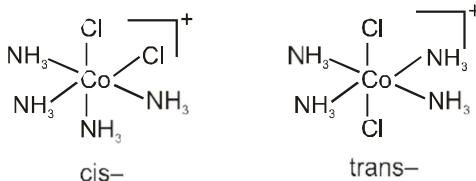


Square planar complex of the type $Mabcd$ (where a, b, c, d are unidentates) shows three geometrical isomers.



Coordination Number Six :

Geometrical isomerism is also possible in octahedral complexes.



Geometrical isomers (cis and trans) of $[Co(NH_3)_3Cl_2]^+$

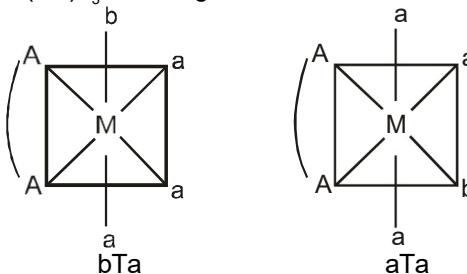
Number of possible isomers and the spatial arrangements of the ligands around the central metal ion for the specific complexes are given below.

(I) Complexes containing only unidentate ligands

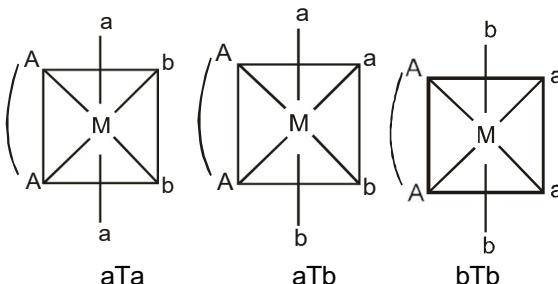
(i) Ma_2b_4 \tilde{n} 2 ; (ii) Ma_4bc \tilde{n} 2 (iii) Ma_3b_3

(II) Compounds containing bidentate ligand and unidentate ligands.

(i) $M(AA)a_3b$ – Two geometrical isomers are possible.

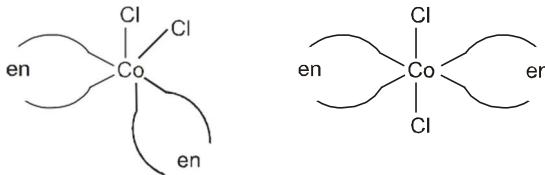


(ii) $M(AA)a_2b_2$ – Three geometrical isomers are possible.



Note : With $[M(AA)b_4]$, only one form is possible. $M(AA)abcd$ have six geometrical isomers.

(iii) $M(AA)_2O_2$ – Two geometrical isomers are possible.



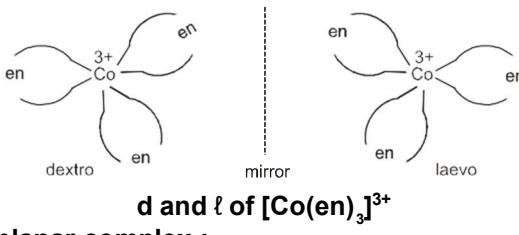
Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

Optical Isomerism :

A coordination compound which can rotate the plane of polarised light is said to be optically active.

Octahedral complex :

Optical isomerism is common in octahedral complexes involving didentate ligands. For example, $[Co(en)_3]^{3+}$ has d and l forms as given below.



d and l of $[Co(en)_3]^{3+}$

Square planar complex :

Square planar complexes are rarely found to show the optical isomerism. The plane formed by the four ligating atoms and the metal ion is considered to be a mirror plane and thus prevents the possibility of chirality.

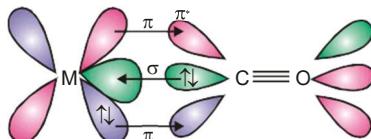
ORGANOMETALLIC COMPOUNDS

METAL CARBONYLS :

Compounds of metals with CO as a ligand are called metal carbonyls. They are of two types.

- (a) **Monomeric** : Those metal carbonyls which contain only one metal atom per molecule are called monomeric carbonyls. For examples : $[Ni(CO)_4]$ (sp^3 , tetrahedral); $[Fe(CO)_5]$ (dsp^3 , trigonal bipyramidal).
- (b) **Polymeric** : Those metal carbonyls which contain two or more than two metal atoms per molecule and they have metal-metal bonds are called polymeric carbonyl. For example : $Mn_2(CO)_{10}$, $Co_2(CO)_9$, etc.

The M—C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. Thus carbon monoxide acts as σ donor (OC \rightarrow M) and a π acceptor (OC \leftarrow M), with the two interactions creating a synergic effect which strengthens the bond between CO and the metal as shown in figure.



Synergic bonding

Sigma (σ) bonded organometallic compounds :

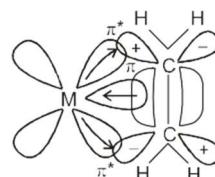
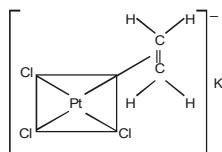
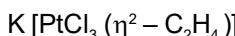
(a) Grignard's Reagent R—Mg—X where R is a alkyl or aryl group and X is halogen.

(b) $(\text{CH}_3)_4\text{Sn}$, $(\text{C}_2\text{H}_5)_4\text{Pb}$, $\text{Al}_2(\text{CH}_3)_6$, $\text{Al}_2(\text{C}_2\text{H}_5)_6$ etc.

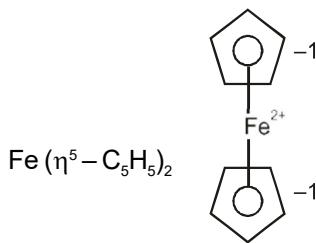
Pi (π)-bonded organometallic compounds :

These are the compounds of metal with alkenes, alkynes, benzene and other ring compounds.

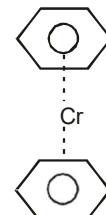
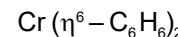
Zeise's salt :



Ferrocene and bis(benzene)chromium :



and



METALLURGY

The compound of a metal found in nature is called a mineral. The minerals from which metal can be economically and conveniently extracted are called **ores**. An ore is usually contaminated with earthy or undesired materials known as gangue.

- (a) **Native ores** contain the metal in free state. Silver, gold, platinum etc, occur as native ores.
- (b) **Oxidised ores** consist of oxides or oxysalts (e.g. carbonates, phosphates, sulphates and silicates) of metals.
- (c) **Sulphurised ores** consist of sulphides of metals like iron, lead, zinc, mercury etc.
- (d) **Halide ores** consist of halides of metals.

| Metal | Ores | Composition |
|-----------|-----------------------------|--|
| Aluminium | Bauxite | $\text{AlO}_x(\text{OH})_{3-2x}$ [where $0 < X < 1$] Al_2O_3 |
| | Diaspore | $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ |
| | Corundam | Al_2O_3 |
| | Kaolinite (a form of clay) | $[\text{Al}_2(\text{OH})_4 \text{Si}_2\text{O}_5]$ |
| Iron | Haematite | Fe_2O_3 |
| | Magnetite | Fe_3O_4 |
| | Siderite | FeCO_3 |
| | Iron pyrite | FeS_2 |
| | Limonite | $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ |
| Copper | Copper pyrite | CuFeS_2 |
| | Copper glance | Cu_2S |
| | Cuprite | Cu_2O |
| | Malachite | $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ |
| | Azurite | $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ |
| Zinc | Zinc blende or Sphalerite | ZnS |
| | Calamine | ZnCO_3 |
| | Zincite | ZnO |
| Lead | Galena | PbS |
| | Anglesite | PbSO_4 |
| | Cerrusite | PbCO_3 |
| Magnesium | Carnallite | $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ($\text{K}_2\text{MgCl}_4 \cdot 6\text{H}_2\text{O}$) |
| | Magnesite | MgCO_3 |
| | Dolomite | $\text{MgCO}_3 \cdot \text{CaCO}_3$ |
| | Epsomsalt (Epsomite) | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ |
| Tin | Langbeinite | $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ |
| | Cassiterite (Tin stone) | SnO_2 |
| Silver | Silver glance (Argentite) | Ag_2S |
| | Chlorargyrite (Horn silver) | AgCl |

Metallurgy :

The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

The isolation and extraction of metals from their ores involve the following major steps:

(A) Crushing and Grinding : The ore is first crushed by jaw crushers and ground to a powder.

(B) Concentration :

The removal of unwanted useless impurities from the ore is called **dressing, concentration or benefaction of ore**.

(i) Hydraulic washing or Gravity separation or Levigation method :

It is based on the difference in the densities of the gangue and ore particles. This method is generally used for the concentration of oxide and native ores.

(ii) Electromagnetic separation :

It is based on differences in magnetic properties of the ore components. Chromite ore($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) is separated from non-magnetic silicious impurities and cassiterite ore(SnO_2) is separated from magnetic Wolframite ($\text{FeWO}_4 + \text{MnWO}_4$).

(iii) Froth floatation process. This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb); copper pyrites $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ or CuFeS_2 (ore of copper) ; zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil. In this process one or more chemical frothing agents are added.

(iv) Leaching : Leaching is often used if the ore is soluble in some suitable solvent, e.g, acids, bases and suitable chemical reagents.

(C) Extraction of crude metal from concentrated ore :

The isolation of metals from concentrated ore involves two major steps as given below.

(i) Conversion to oxide :

Calcination. It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of calcination brings about the following changes :

(a) The carbonate ore gets decomposed to form the oxide of the metal.

(b) Water of crystallisation present in the hydrated oxide ore gets lost as moisture.

(c) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

Roasting :

It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or O_2 below its melting point. Roasting is an exothermic process once started it does not require additional heating.

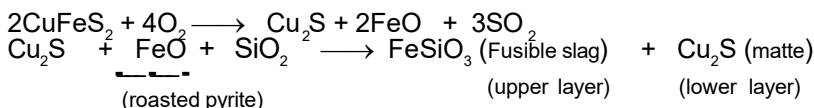
Smelting :

Slag formation : In many extraction processes, an oxide is added deliberately to combine with other impurities and form a stable molten phase immiscible with molten metal called a slag. The process is termed smelting.

The principle of slag formation is essentially the following :

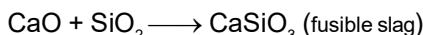
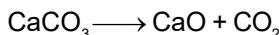
Nonmetal oxide (acidic oxide) + Metal oxide (basic oxide) \longrightarrow Fusible (easily melted) slag

Removal of unwanted basic and acidic oxides: For example, FeO is the impurity in extraction of Cu from copper pyrite.



Matte also contains a very small amount of iron(II) sulphide.

To remove unwanted acidic impurities like sand and P_4O_{10} , smelting is done in the presence of limestone.



(ii) Reduction of a metal oxide :

The free metal is obtained by reduction of a compound, using either a chemical reducing agent or electrolysis.

Chemical reduction method :

Reduction with carbon :



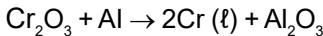
Reduction with CO : In some cases CO produced in the furnace itself is used as a reducing agent.



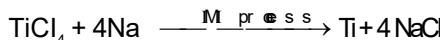
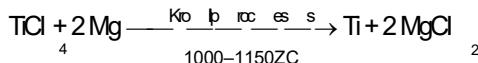
Reduction by other metals :

Metallic oxides (Cr and Mn) can be reduced by a highly electropositive metal such as aluminium that liberates a large amount of energy (1675 kJ/mol) on oxidation to Al_2O_3 . The process is known as Goldschmidt or

aluminothermic process and the reaction is known as thermite reaction.

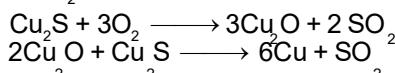


Magnesium reduction method : Magnesium is used in similar way to reduce oxides. In certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce halides.



Self-reduction method :

This method is also called auto-reduction method or air reduction method. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb, Sb, etc. are heated in air, a part of these is changed into oxide or sulphate then that reacts with the remaining part of the sulphide ore to give its metal and SO_2 .



Electrolytic reduction :

It presents the most powerful method of reduction and gives a very pure product. As it is an expensive method compared to chemical methods, it is used either for very reactive metals such as magnesium or aluminum or for production of samples of high purity.

- In aqueous solution :** Electrolysis can be carried out conveniently and cheaply in aqueous solution that the products do not react with water. Copper and zinc are obtained by electrolysis of aqueous solution of their sulphates.
- In fused melts :** Aluminum is obtained by electrolysis of a fused mixture of Al_2O_3 and cryolite $\text{Na}_3[\text{AlF}_6]$.

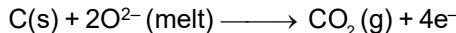
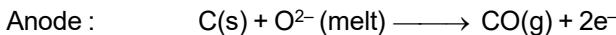
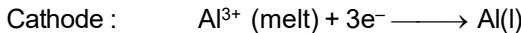
Extraction of Aluminium :

It involves the following processes

(a) Purification of bauxite :

| (i) Bayer's Method (used for red bauxite containing Fe_2O_3 and silicates as impurities) | (ii) Hall's Method (used for red bauxite containing Fe_2O_3 and silicates as impurities) | (iii) Serpeck's Method (used for white bauxite containing silica as impurities) |
|--|--|--|
| $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \xrightarrow[8\text{ min}]{190^\circ\text{C}}$ $2\text{NaAlO}_2 \text{ (soluble)} + 3\text{H}_2\text{O}$ $\text{Fe}_2\text{O}_3 \text{ (insoluble)} \text{ separated as red mud by filtration}$ <p>solution is diluted with water and seeded with freshly prepared $\text{Al}(\text{OH})_3$. It induces the precipitation of $\text{Al}(\text{OH})_3$. $\text{Al}(\text{OH})_3$ is filtered leaving behind silicates in solution.</p> $\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NaOH} + \text{Al}(\text{OH})_3 \downarrow$ $2\text{Al}(\text{OH})_3 \xrightarrow{1473\text{K}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$ | $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \xrightarrow{\text{Fuse}}$ $2\text{NaAlO}_2 \text{ (soluble)} + \text{CO}_2 + 2\text{H}_2\text{O}$ $2\text{NaAlO}_2 + 3\text{H}_2\text{O} + \text{CO}_2 \xrightarrow{60^\circ\text{C}}$ $2\text{Al}(\text{OH})_3 \downarrow + \text{Na}_2\text{CO}_3$ $2\text{Al}(\text{OH})_3 \xrightarrow{1473\text{K}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$ | $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 3\text{C} + \text{N}_2 \xrightarrow[1800^\circ\text{C}]{\text{Electric furnace}}$ $2\text{AlN} + 3\text{CO} + 2\text{H}_2\text{O}$ $2\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 \downarrow + \text{NH}_3$ $\text{SiO}_2 + 2\text{CO} \rightarrow 2\text{CO}_2 + \text{Si}$ <p>Silicon volatilises at this temp.</p> $2\text{Al}(\text{OH})_3 \xrightarrow{1473\text{K}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$ |

(b) Electrolytic reduction (Hall-Heroult process) :

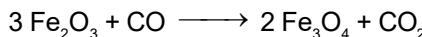


Metallurgy of some important metals

1. Extraction of iron from ore haematite :

Reactions involved :

At 500 – 800 K (lower temperature range in the blast furnace)



At 900 – 1500 K (higher temperature range in the blast furnace):

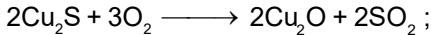
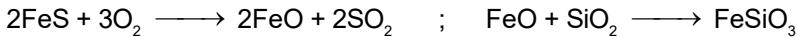


Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.

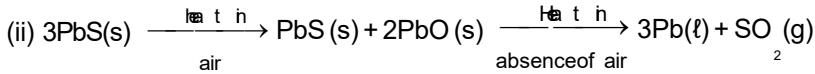


2. Extraction of copper :

From copper glance / copper pyrite (self reduction) :



3. Extraction of lead :

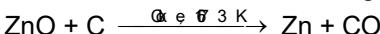


4. Extraction of zinc from zinc blende :

The ore is roasted in presence of excess of air at temperature 1200 K.



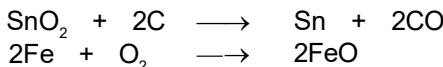
The reduction of zinc oxide is done using coke.



5. Extraction of tin from cassiterite :

The concentrated ore is subjected to the electromagnetic separation to remove magnetic impurity of Wolframite.

SnO_2 is reduced to metal using carbon at 1200–1300°C in an electric furnace. The product often contains traces of Fe, which is removed by blowing air through the molten mixture to oxidise FeO which then floats to the surface.



6. Extraction of Magnesium :

From Sea water (Dow's process) :

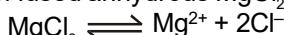
Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

- (a) Precipitation of magnesium as magnesium hydroxide by slaked lime.
- (b) Preparation of hexahydrated magnesium chloride.

The solution on concentration and crystallisation gives the crystals of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

(c) Preparation of anhydrous magnesium chloride.

(d) Electrolysis of fused anhydrous MgCl_2 in presence of NaCl .

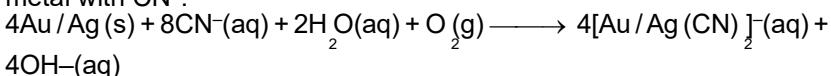


At cathode : $\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$ (99% pure) ;

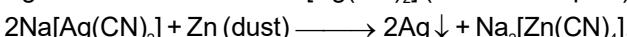
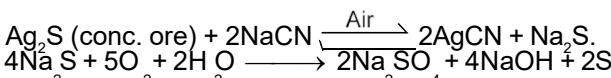
At anode : $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$

7. Extraction of gold and silver (MacArthur-Forrest cyanide process) :

(a) From native ores : Extraction of gold and silver involves leaching the metal with CN^- .



(b) From argentite ore :



(D) **Purification or Refining of metals :**

Physical methods : These methods include the following processes:

(I) Liquation process : This process is used for the purification of the metal, which itself is readily fusible, but the impurities present in it are not, used for the purification of Sn and Zn, and for removing Pb from Zn-Ag alloy.

(II) Fractional distillation process : This process is used to purify those metals which themselves are volatile and the impurities in them are nonvolatile and vice-versa. Zn, Cd and Hg are purified by this process.

(III) Zone refining method (Fractional crystallisation method) : This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors

Chemical methods : These methods include the following methods:

(I) OXIDATIVE REFINING :

This method is usually employed for refining metals like Pb, Ag, Cu, Fe, etc. In this method the molten impure metal is subjected to oxidation by various ways.

(II) POLING PROCESS :

This process is used for the purification of copper and tin which contains the impurities of their own oxides.

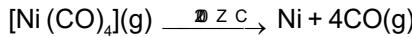
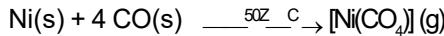
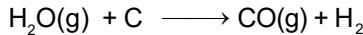


(III) ELECTROLYTIC REFINING :

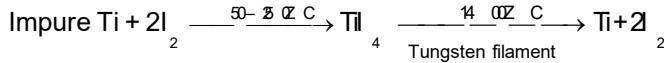
Some metals such as Cu, Ni, and Al are refined electrolytically.

(IV) VAPOR PHASE REFINING :

(i) Extraction of Nickel (Mondís process) : The sequence of reaction is



(ii) Van Arkel-De Boer process :



s-BLOCK ELEMENTS & THEIR COMPOUNDS

Group 1 of the periodic table consists of the elements : lithium, sodium, potassium, rubidium, caesium and francium .

The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium.

Hydration Enthalpy :

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes. Li^+ has maximum degree of hydration and for this reasons lithium salts are mostly hydrated e.g., $\text{LiCl} \cdot 2\text{H}_2\text{O}$

Physical properties :

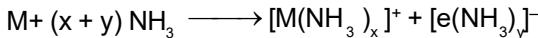
All the alkali metal are silvery white, soft and light metals. Because of the larger size, these element have low density. The melting and boiling point of the alkali metals are low indicating weak metallic bonding alkali metals and their salts impart characteristic colour to an oxidizing flame.

| Metal | Li | Na | K | Rb | Cs |
|--------|-------------|--------|---------------|------------|------|
| Colour | Crimson red | Yellow | Violet/ Lilac | Red violet | Blue |

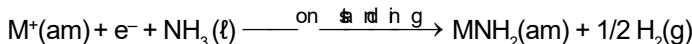
Chemical Properties:

The alkali metal are highly reactive due to their larger size and low ionization enthalpy.

- **Reactivity towards air :** They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxide.
- **Reducing nature:** The alkali metals, are strong reducing agents, lithium being the most and sodium the least powerful.
- **Solution in liquid ammonia:** The alkali metals dissolve in liquid ammonia giving deep blue solution which are conducting in nature.



The blue colour of the solution is due to the ammoniated electron and the solutions is paramagnetic.



In concentrated solution, the blue colour changes to bronze colour and becomes, diamagnetic.

ANOMALOUS PROPERTIES OF LITHIUM

(i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/ radius ratio).

The similarity between lithium and magnesium is particularly striking and arises because of their similar size: atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : Li⁺ = 76 pm, Mg²⁺ = 72 pm.

GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The first element beryllium differs from the rest of the member and shows diagonal relationship to aluminium.

Hydration Enthalpies

Hydration enthalpies of alkaline earth metal ions. Be²⁺ > Mg²⁺ > Ca²⁺ > Sr²⁺ > Ba²⁺. The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals , e.g., MgCl₂ and CaCl₂ exist as MgCl₂.6H₂O and CaCl₂. 6H₂O while NaCl and KCl do not form such hydrates.

Physical Properties

The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. The melting and boiling point of these metals are higher due to smaller sizes. Because of the low ionisation enthalpies they are strongly electropositive in nature. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence these elements do not impart any colour to the flame.

Calcium, strontium and barium impart characteristic colour to the flame.

| Me tal | Be | Mg | Ca | Sr | Ba |
|--------|-----------|-----------|-----------|---------|-------------|
| Colour | No colour | No colour | Brick red | Crimson | Apple green |

Chemical Properties

○ **Reactivity towards air and water :** Beryllium and magnesium are inert to oxygen and water. Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg₃N₂. Calcium, strontium and barium are readily attacked by air to form the oxide and nitride.

○ **Reducing nature :** The alkaline earth metals are strong reducing agent. This is indicated by large negative value of their reduction potentials.

○ **Solution in liquid ammonia:** The alkaline earth metals dissolve in liquid ammonia to give deep blue black solution forming ammoniated ions.



From these solutions, the ammoniates, $[M(\text{NH}_3)]^{2+}$ can be recovered.

ANOMALOUS BEHAVIOUR OF BERYLLIUM

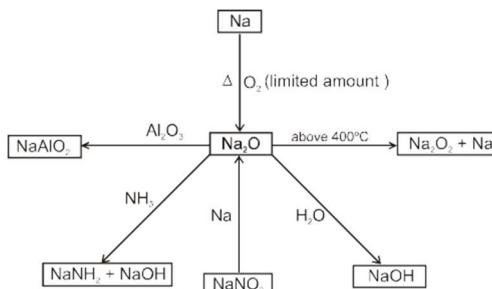
Beryllium the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium.

Diagonal Relationship between Beryllium and Aluminium

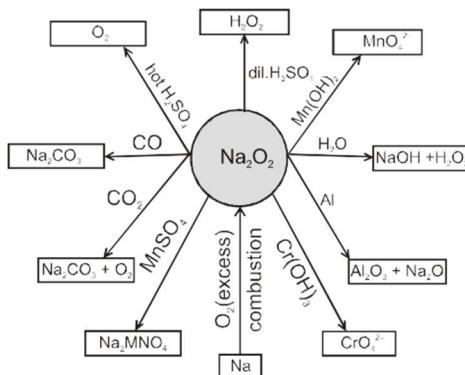
The ionic radius of Be^{2+} is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways.

Compounds of s-block elements :

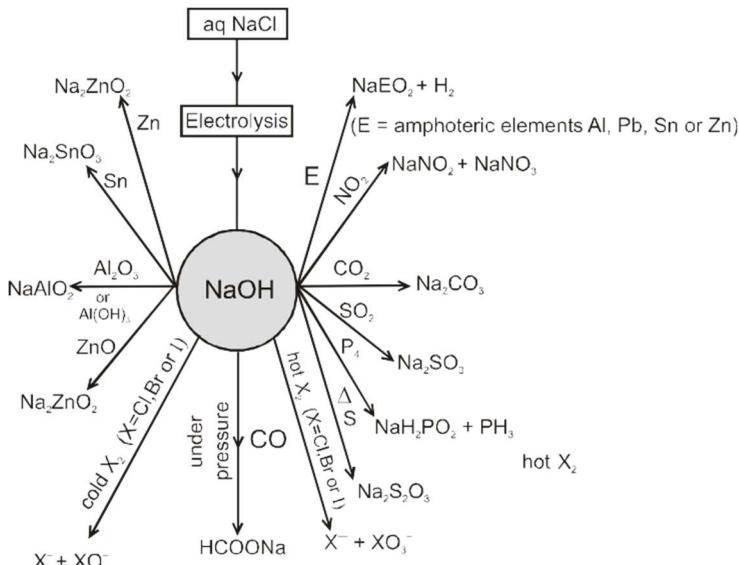
1. Sodium Oxide (Na_2O) :



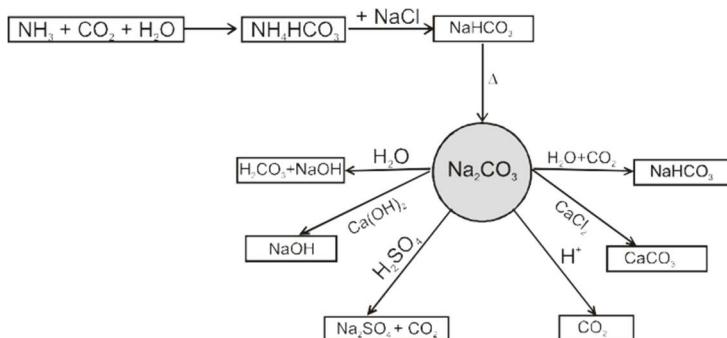
2. Sodium peroxide (Na_2O_2) :



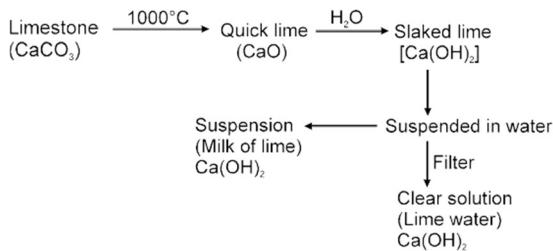
3. Sodium Hydroxide (NaOH) :

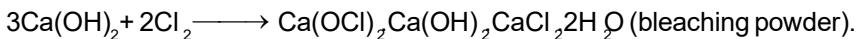
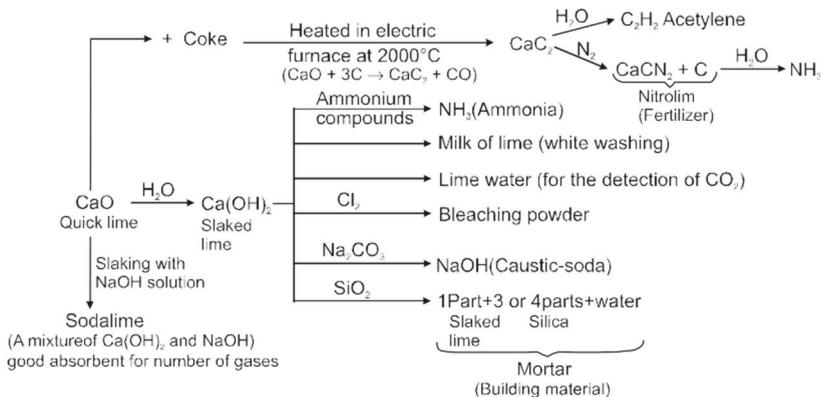


4. Sodium Carbonate (Na₂CO₃) :



5. Quick Lime, Slaked Lime and Lime Water :





p-BLOCK ELEMENTS & THEIR COMPOUNDS

TRENDS IN PROPERTIES OF p-BLOCK ELEMENTS.

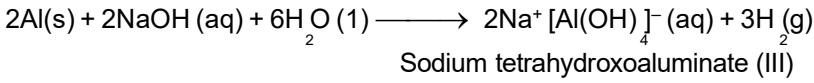
| Electronegativity, ionization enthalpy, oxidizing power. | | | | | | |
|--|----|----|----|----|----|----|
| | B | C | N | O | F | Ne |
| Covalent radius, van der Waals' radius, metallic character | Al | Si | P | S | Cl | Ar |
| | Ga | Ge | As | Se | Br | Kr |
| | In | Sn | Sb | Te | I | Xe |
| | Tl | Pb | Bi | Po | At | Rn |
| Covalent radius, van der Waals' radius, enthalpy of atomization (upto group 14), metallic character | | | | | | |
| Electronegativity, enthalpy of atomization (except for N ₂ , O ₂ , F ₂), ionization enthalpy, oxidizing power. | | | | | | |

(A) GROUP 13 ELEMENTS : THE BORON FAMILY

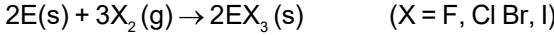
Oxidation state and trends in chemical reactivity :

General Oxidation State = + 3.

Reactivity towards acids and alkalies

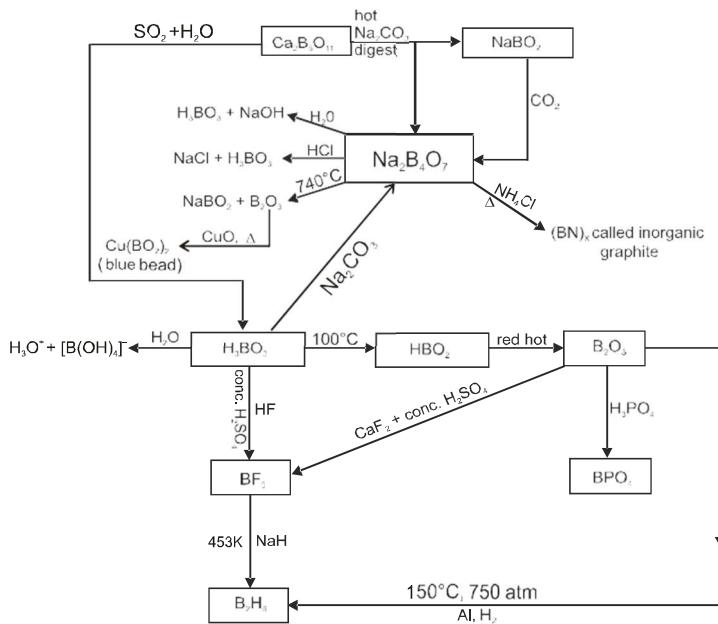
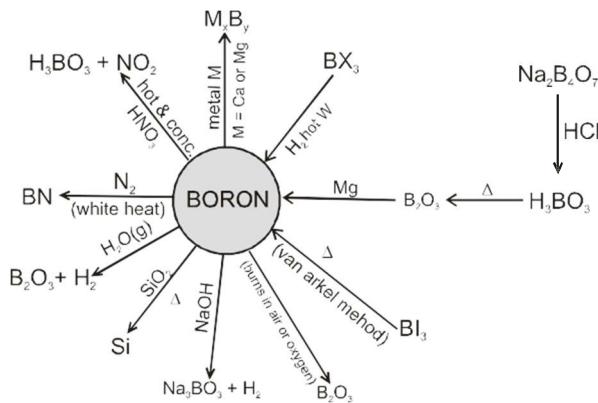


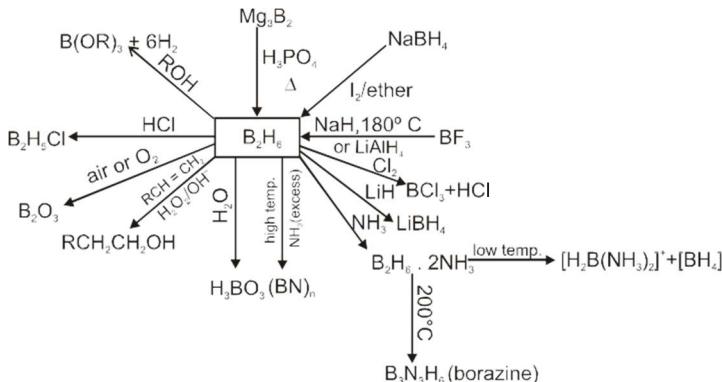
Reactivity towards halogens



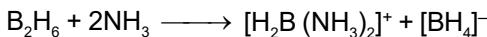
BORON (B):

Some Important Reactions of Boron and its compounds :

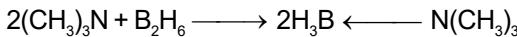




- Small amines such as NH_3 , CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$ give unsymmetrical cleavage of diborane.



- Large amines such as $(\text{CH}_3)_3\text{N}$ and pyridine give symmetrical cleavage of diborane.



- $\text{B}_2\text{H}_6 + 2\text{CO} \xrightarrow{20^\circ\text{C}, 2\text{ atm}} 2\text{BH}_3\text{CO}$ (borane carbonyl)

(B) GROUP 14 ELEMENTS : THE CARBON FAMILY

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14.

Electronic Configuration = $ns^2 np^2$.

Oxidation states and trends in chemical reactivity

Common oxidation states = +4 and +2. Carbon also exhibits negative oxidation states. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb.

(i) Reactivity towards oxygen :

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e. monoxide and dioxide of formula MO and MO_2 respectively.

(ii) Reactivity towards water :

Tin decomposes steam to form dioxide and dihydrogen gas.

(iii) Reactivity towards halogen :

These elements can form halides of formula MX_2 and MX_4 (where $\text{X} = \text{F, Cl, Br, I}$). Stability of dihalides increases down the group.

ANOMALOUS BEHAVIOUR OF CARBON :

Catenation :

The order of catenation is C > > Si > Ge \approx Sn. Lead does not show catenation. Due to the property of catenation and $p\pi$ - $p\pi$ bonds formation, carbon is able to show allotropic forms.

| Bond | Bond enthalpy (kJ mol ⁻¹) | Bond | Bond enthalpy (kJ mol ⁻¹) |
|-------|---------------------------------------|-------|---------------------------------------|
| C—C | 348 | Si—Si | 297 |
| Ge—Ge | 260 | Sn—Sn | 240 |

Allotropes of Carbon

Diamond :

Crystalline lattice sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral manner. The C—C bond length is 154 pm. and produces a rigid three dimensional network of carbon atoms.

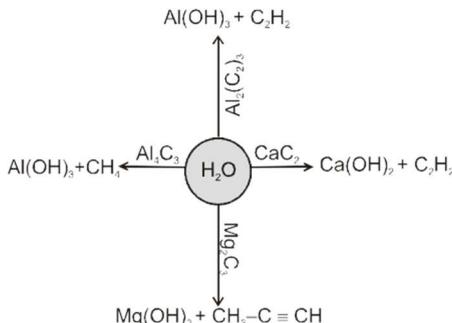
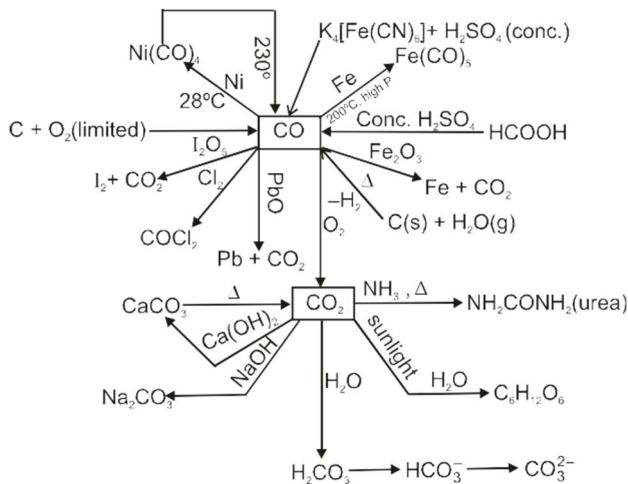
Graphite :

Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C – C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature.

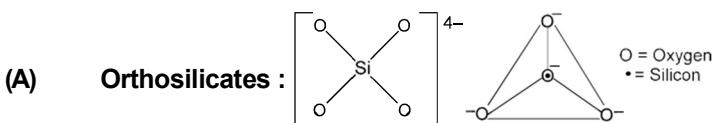
Fullerenes :

C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene**. It contains twenty six -membered rings and twelve five membered rings. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C – C distance of 143.5 pm and 138.3 pm respectively.

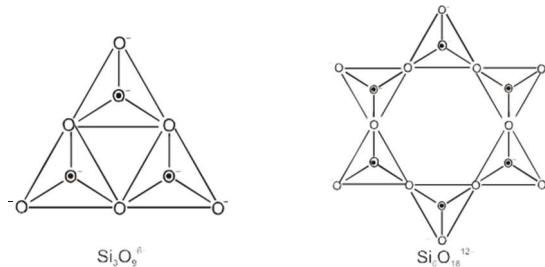
SOME IMPORTANT REACTIONS OF CO, CO₂ AND METAL CARBIDES :



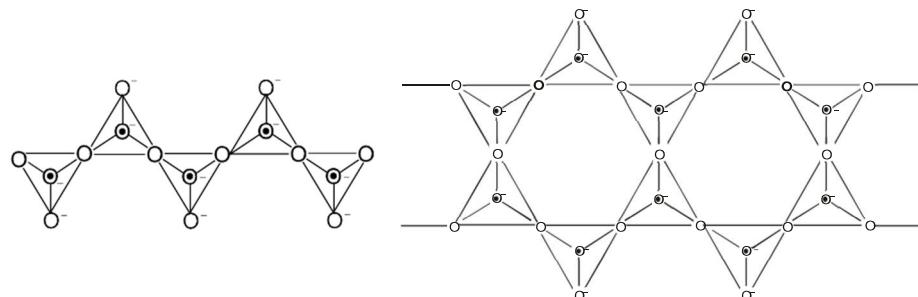
● CLASSIFICATION OF SILICATES :



(C) Cyclic silicates :



(D) Chain silicates :



(E) Two dimensional sheet silicates :

In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedrals. Such sharing forms two dimension sheet structure with general formula $(\text{Si}_2\text{O}_5)_n^{2n-}$

(F) Three dimensional sheet silicates :

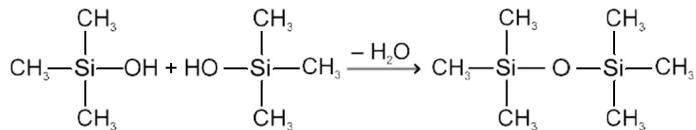
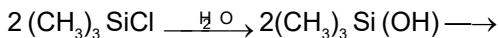
These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} tetrahedral units.

● **SILICONES :**

☞ Silicones can be prepared from the following types of compounds only.

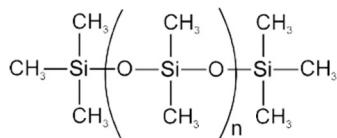


☞ Silicones from the hydrolysis of $(\text{CH}_3)_3\text{SiCl}$





Silicones from the hydrolysis of a mixture of $(\text{CH}_3)_3\text{SiCl}$ & $(\text{CH}_3)_2\text{SiCl}_2$



- When a compound like CH_3SiCl_3 undergoes hydrolysis, a complex cross-linked polymer is obtained.
- The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent.

(C) GROUP 15 ELEMENTS : *THE NITROGEN FAMILY*

Electronic Configuration : $\text{ns}^2 \text{np}^3$

Atomic and Ionic Radii : Covalent and ionic (in a particular state) radii increase in size down the group.

Physical Properties:

All the elements of this group are polyatomic. Metallic character increases down the group. The boiling points , in general , increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen , all the elements show allotropy.

Chemical Properties :

Oxidation States and trends in a chemical reactivity :

The common oxidation states of these elements are -3 , $+3$ and $+5$. The stability of $+5$ oxidation state decreases and that of $+3$ state increases (due to inert pair effect) down the group ; $\text{Bi}^{3+} > \text{Sb}^{3+} > \text{As}^{3+}$; $\text{Bi}^{5+} < \text{Sb}^{5+} < \text{As}^{5+}$

Nitrogen exhibits $+1$, $+2$, $+4$ oxidation states also when it reacts with oxygen.

Anomalous properties of nitrogen :

(i)

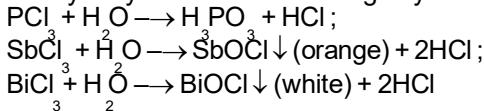
The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently , the reducing character of the hydrides increases. Basicity also decreases in the order $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 \geq \text{BiH}_3$.

PROPERTIES OF HYDRIDES OF GROUP 15 ELEMENTS

| Property | NH ₃ | PH ₃ | AsH ₃ | SbH ₃ | BiH ₃ |
|--|-----------------|-----------------|------------------|------------------|------------------|
| Melting point / K | 195.2 | 139.5 | 156.7 | 185 | – |
| Boiling point / K | 238.5 | 185.5 | 210.6 | 254.6 | 290 |
| (E – H) Distance / pm | 101.7 | 141.9 | 151.9 | 170.7 | – |
| HEH angle (°) | 107.8 | 93.6 | 91.8 | 91.3 | – |
| Δ _f H° / kJ mol ⁻¹ | – 46.1 | 13.4 | 66.4 | 145.1 | 278 |
| Δ _{diss} H°(E – H) / kJ mol ⁻¹ | 389 | 322 | 297 | 255 | – |

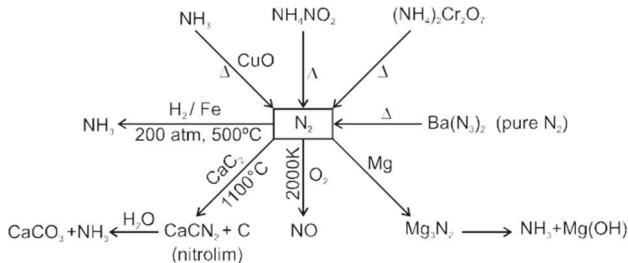
(ii) The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E₂O₃ of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

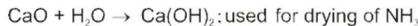
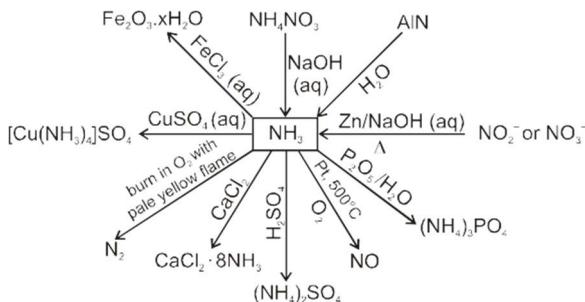
(iii) Nitrogen does not form pentahalide due to non – availability of the d-orbitals in its valence shell. Pentahalides are more covalent than trihalides. Halides are hydrolysed in water forming oxyacids or oxychlorides.



(iv) These elements react with metals to form their binary compounds exhibiting –3 oxidation state, such as, Ca₃N₂ (calcium nitride) Ca₃P₂ (calcium phosphide) and Na₃As₂ (sodium arsenide).

NITROGEN (N) AND ITS COMPOUNDS :

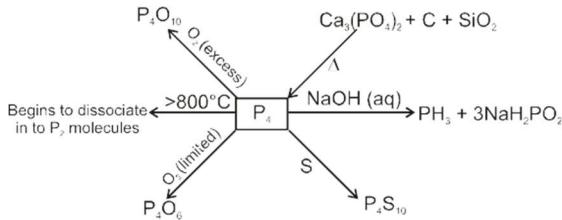




Oxides of Nitrogen

| Name | Formula | Oxidation state of nitrogen | Common methods of preparation | Physical appearance and chemical nature |
|--|-------------------------------|-----------------------------|--|---|
| Dinitrogen oxide [Nitrogen(I) oxide] | N ₂ O | + 1 | $\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2 \text{H}_2\text{O}$ | colourless gas , neutral |
| Nitrogen monoxide [Nitrogen(II) oxide] (Nitric acid) | NO | + 2 | $2 \text{NaNO}_2 + 2 \text{FeSO}_4 + 3 \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2 \text{NaHSO}_4 + 2 \text{H}_2\text{O} + 2 \text{NO}$ | colourless gas , neutral |
| Dinitrogen trioxide [Nitrogen(III) oxide] (Nitrogen sesquioxide) | N ₂ O ₃ | + 3 | $2 \text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250 \text{ K}} 2 \text{N}_2\text{O}_3$ | blue solid , acidic |
| Nitrogen dioxide [Nitrogen(IV) oxide] | NO ₂ | + 4 | $2 \text{Pb}(\text{NO}_3)_2 \xrightarrow{673 \text{ K}} 4 \text{NO}_2 + 2 \text{PbO} + \text{O}_2$ | brown gas, acidic |
| Dinitrogen tetraoxide [Nitrogen(IV) oxide] | N ₂ O ₄ | + 4 | $2 \text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{cool}} \text{N}_2\text{O}_4$ | colourless solid / liquid , acidic |
| Dinitrogen pentoxide [Nitrogen(V) oxide] | N ₂ O ₅ | + 5 | $4 \text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow 4 \text{HPO}_3 + 2 \text{N}_2\text{O}_5$ | colourless solid, acidic |

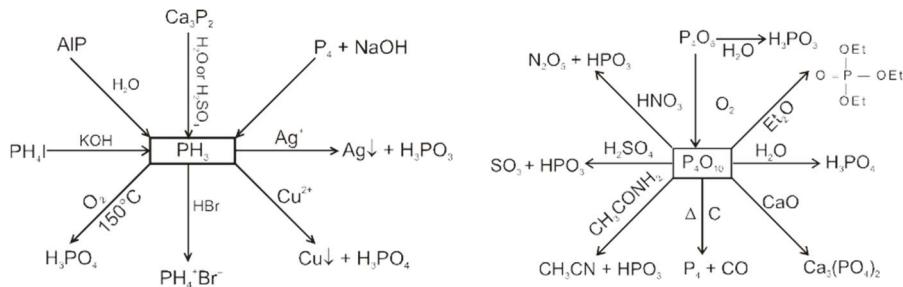
PHOSPHORUS (P) AND ITS COMPOUNDS :



When white phosphorus is heated in the atmosphere of CO_2 or coal gas at 573 K red phosphorus is produced.

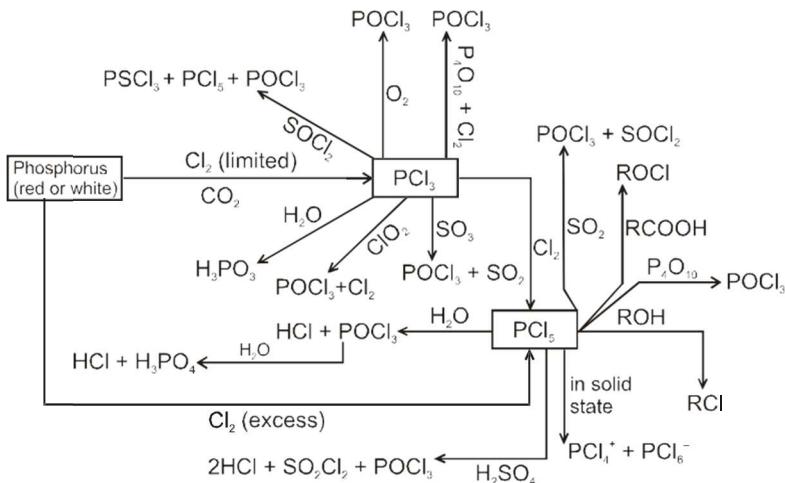
α -black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K. β -black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.

Order of thermodynamic stability of various allotropes of phosphorus : black > red > white



Oxoacids of Phosphorus

| Name | Formula | Oxidation state of phosphorus | Characteristic bonds and their number | Preparation |
|------------------|----------------------------------|-------------------------------|---|---|
| Hypophosphorous | H_3PO_2 | + 1 | One $\text{P} - \text{OH}$ Two $\text{P} - \text{H}$ One $\text{P} = \text{O}$ | white $\text{P}_4 + \text{alkali}$ |
| Orthophosphorous | H_3PO_3 | + 3 | Two $\text{P} - \text{OH}$ One $\text{P} - \text{H}$ One $\text{P} = \text{O}$ | $\text{P}_2\text{O}_3 + \text{H}_2\text{O}$ |
| Pyrophosphorous | $\text{H}_4\text{P}_2\text{O}_5$ | + 3 | Two $\text{P} - \text{OH}$ Two $\text{P} - \text{H}$ Two $\text{P} = \text{O}$ | $\text{PCl}_3 + \text{H}_3\text{PO}_3$ |
| Hypophosphoric | $\text{H}_4\text{P}_2\text{O}_6$ | + 4 | Four $\text{P} - \text{OH}$ Two $\text{P} = \text{O}$ One $\text{P} - \text{P}$ | red $\text{P}_4 + \text{alkali}$ |
| Orthophosphoric | H_3PO_4 | + 5 | Three $\text{P} - \text{OH}$ One $\text{P} = \text{O}$ | $\text{P}_4\text{O}_{10} + \text{H}_2\text{O}$ |
| Pyrophosphoric | $\text{H}_4\text{P}_2\text{O}_7$ | + 5 | Four $\text{P} - \text{OH}$ Two $\text{P} = \text{O}$ One $\text{P} - \text{O} - \text{P}$ | heat phosphoric acid |
| Metaphosphoric | $(\text{HPO}_3)_3$ | + 5 | Three $\text{P} - \text{OH}$ Three $\text{P} = \text{O}$ Three $\text{P} - \text{O} - \text{P}$ | phosphorus acid + Br_2 , heat in sealed tube |



(D) GROUP 16 ELEMENTS : THE OXYGEN FAMILY

Electronic Configuration : $ns^2 np^4$.

Atomic and Ionic Radii :

Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atoms is however, exceptionally small.

Physical Properties :

Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). The melting and boiling points increase with an increase in atomic number down the group.

Catenation :

Tendency for catenation decreases down the group. This property is prominently displayed by sulphur (S_8). The S—S bond is important in biological system and is found in some proteins and enzymes such as cysteine.

Chemical Properties

Oxidation states and trends in chemical reactivity :

Elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common.

Anomalous behaviour of oxygen :

The anomalous behaviour of oxygen is due to its small size and high electronegativity. The absence of d orbitals in oxygen limits its covalency to four.

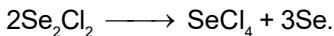
(i) Their acidic character increases from H_2O to H_2Te . The increase in acidic character can be understood in terms of decrease in bond (H-E) dissociation enthalpy down the group. Owing to the decrease in bond (H-E) dissociation enthalpy down the group , the thermal stability of hydrides also decreases from H_2O to H_2Po . All the hydrides except water possess reducing property and this property increases from H_2S to H_2Te .

PROPERTIES OF HYDRIDES OF GROUP 16 ELEMENTS

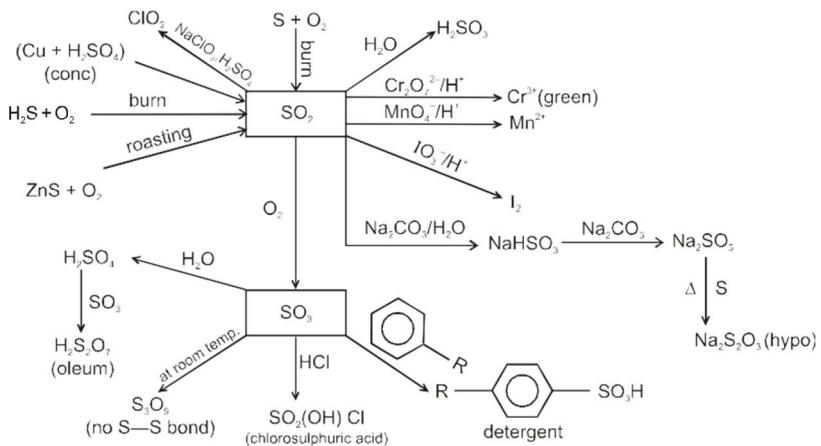
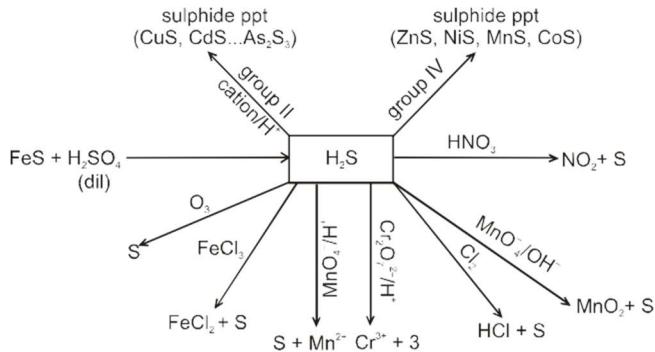
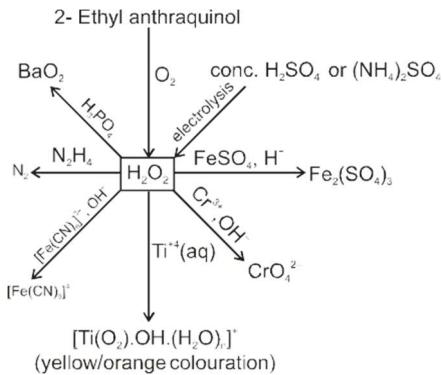
| Property | H_2O | H_2S | H_2Se | H_2Te |
|---|-----------------------|----------------------|-----------------------|-----------------------|
| m.p./K | 273 | 188 | 208 | 222 |
| b.p./K | 373 | 213 | 232 | 269 |
| H-E distance/pm | 96 | 134 | 146 | 169 |
| HEH angle (Z) | 104 | 92 | 91 | 90 |
| $\Delta_f\text{H}/\text{kJ mol}^{-1}$ | -286 | -20 | 73 | 100 |
| $\Delta_{\text{diss}}\text{H (H-E)}/\text{kJ mol}^{-1}$ | 463 | 347 | 276 | 238 |
| Dissociation constant ^a | 1.8×10^{-16} | 1.3×10^{-7} | 1.3×10^{-4} | 2.3×10^{-3} |

(ii) Reducing property of dioxide decreases from SO_2 to TeO_2 ; SO_2 is reducing while TeO_2 is an oxidising agent. Oxides are generally acidic in nature.

(iii) The stabilities of the halides decrease in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$. Sulphur hexafluoride SF_6 is exceptionally stable for steric reasons. 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 :

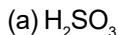


OXYGEN (O_2) AND ITS COMPOUNDS :



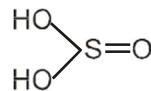
Oxo-acids of Sulphur

1. Suplhurous acid series

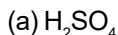


S (IV)

sulphurous acid

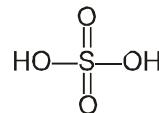


2. Sulphuric acid series

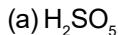


S (VI)

sulphuric acid

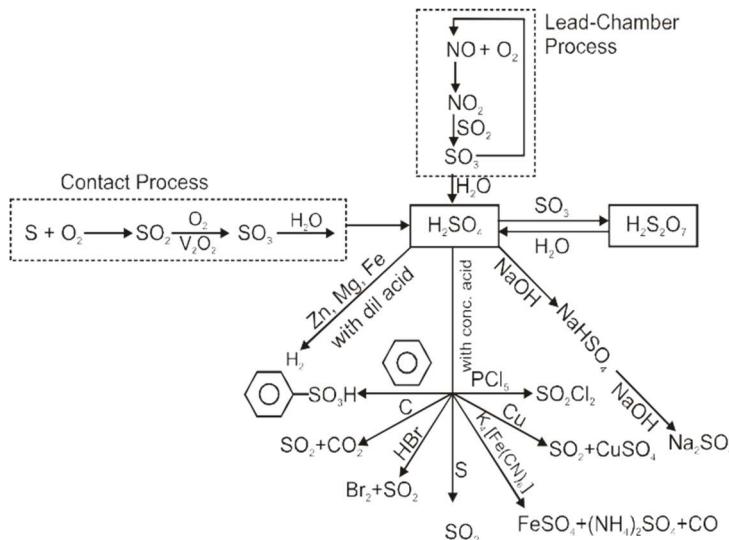
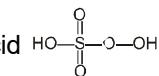


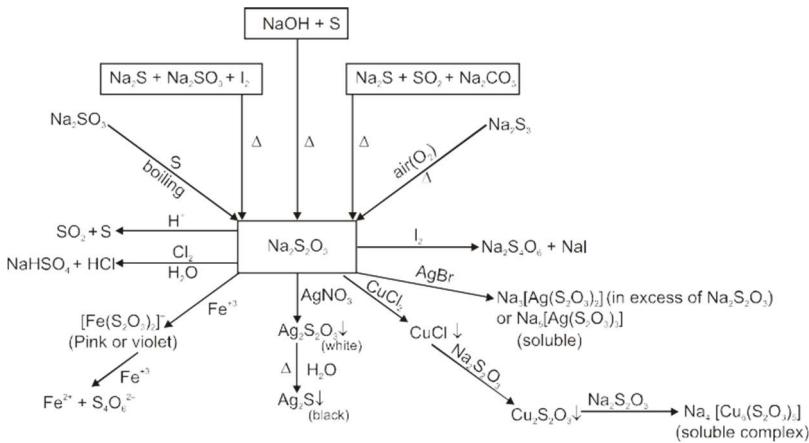
3. Peroxo acid series



S (VI)

peroxomonosulphuric acid (Caro, acid)





(E) GROUP 17 ELEMENTS : THE HALOGEN FAMILY

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17.

Electronic Configuration : $ns^2 np^5$

Atomic and Ionic Radii

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge .

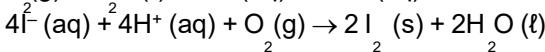
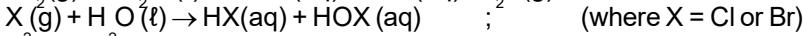
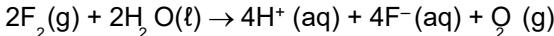
Physical Properties

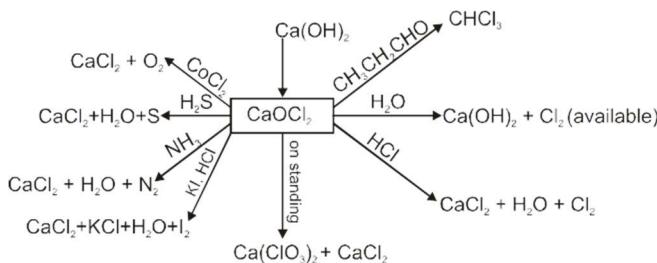
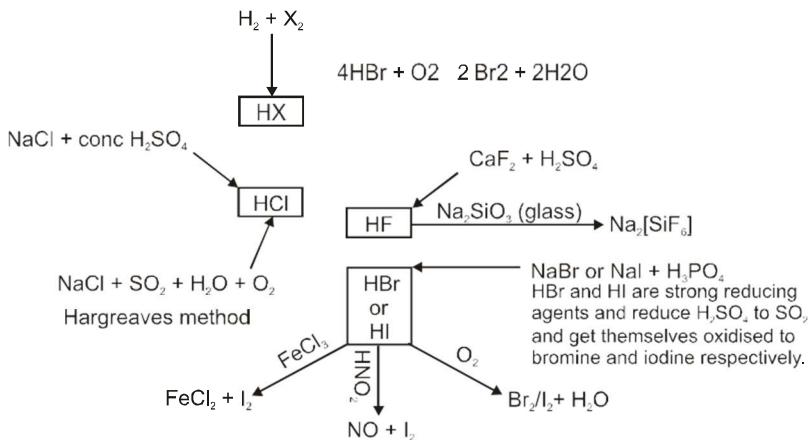
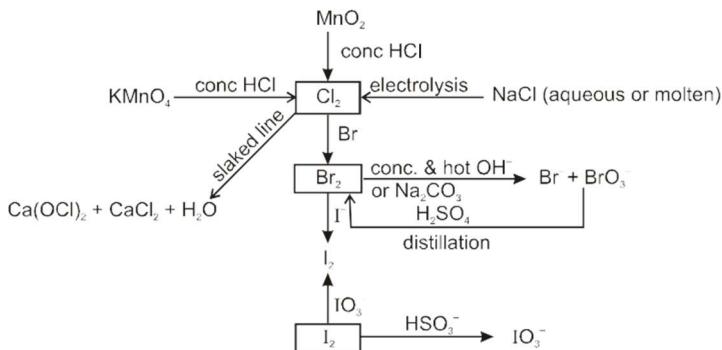
Fluorine and chlorine are gases, bromine is a liquid whereas iodine is a solid. Their melting and boiling points steadily increase with atomic number. The X-X bond disassociation enthalpies from chlorine onwards show the expected trend : $Cl - Cl > Br - Br > F - F > I - I$.

Chemical Properties

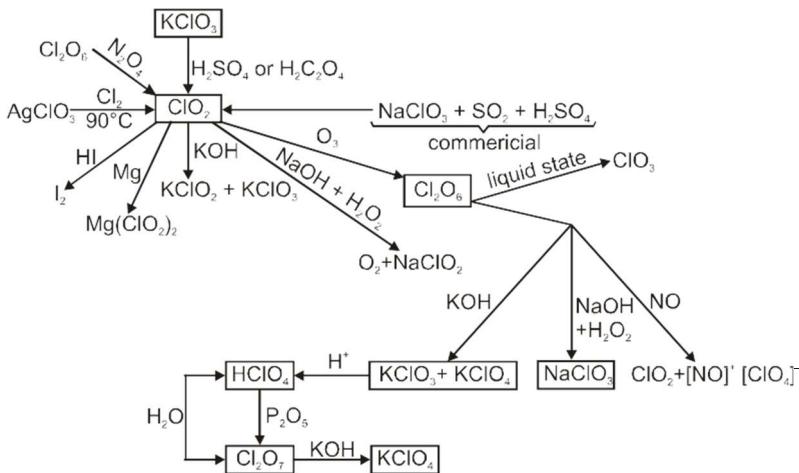
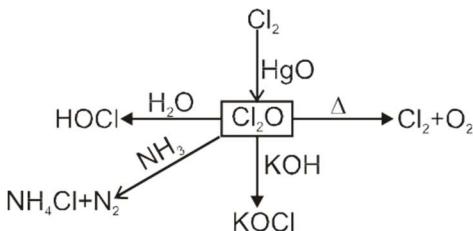
Oxidation states and trends in chemical reactivity

All the halogens exhibit -1 oxidation state. However, chlorine, bromine and iodine exhibit $+1$, $+3$, $+5$ and $+7$ oxidation states also.





*The composition of bleaching powder is Ca(OCl)₂. CaCl₂. Ca(OH)₂. 2H₂O.



(F) GROUP 18 ELEMENTS : (THE ZERO GROUP FAMILY)

Helium, neon, argon, krypton , xenon and radon .

- Most abundant element in air is Ar. Order of abundance in the air is Ar > Ne > Kr > He > Xe.

Electronic Configuration : ns^2np^6

Atomic Radii

Atomic radii increase down the group with increase in atomic number.

Physical properties

All the noble gases are mono-atomic. They are colourless, and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.,

Chemical Properties :

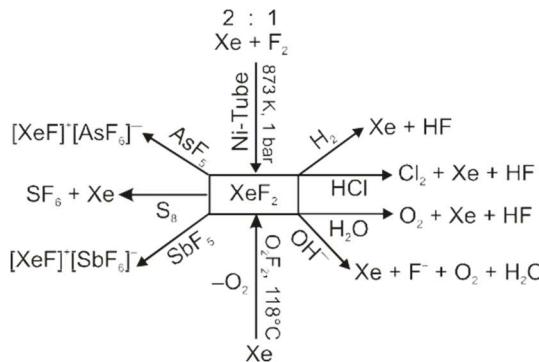
In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

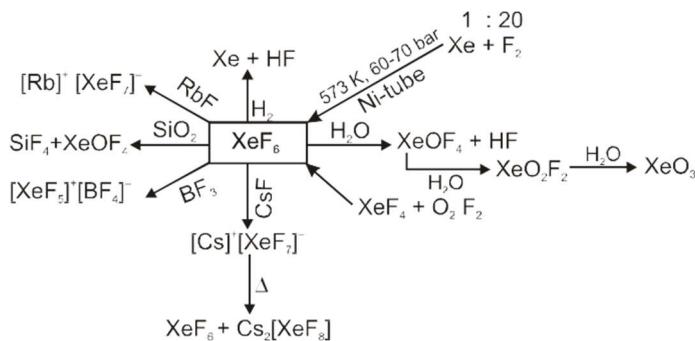
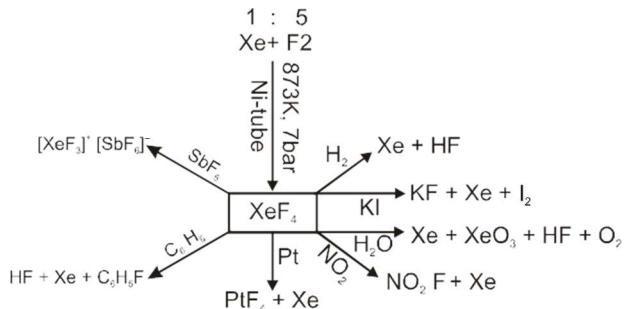
- (i) The noble gases except helium ($1s^2$) have completely filled ns^2 np^6 electronic configuration in their valence shell.
- (ii) They have high ionisation enthalpy and more positive electron gain enthalpy. The reactivity of noble gases has been investigated occasionally ever since their discovery, but all attempt to force them to react to form the compounds were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+ PtF_6^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ mol^{-1}) was almost identical with that xenon (1170 kJ mol^{-1}). He made efforts to prepare same type of compound with $Xe^+ PtF_6^-$ by mixing PtF_6^- and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.
- If Helium is compressed and liquified it forms He(I) liquid at 4.2 K . This liquid is a normal liquid like any other liquid. But if it is further cooled then He(II) is obtained at 2.2 K , which is known as super fluid, because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity & very low viscosity.

Clathrate compounds :

During the formation of ice Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal structure of ice. Compounds thus obtained are called clathrate compounds.

Clathrate provides a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.





d-BLOCK ELEMENTS & THEIR COMPOUNDS

The general electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{0-2}$, where n is the outer most shell.

GENERAL TRENDS IN THE CHEMISTRY OF TRANSITION ELEMENTS.

Metallic character :

Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre. With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

The transition elements (with the exception of Zn, Cd and Hg) are very much hard and have low volatility.

Melting and boiling points :

The melting and boiling points of the transition series elements are generally very high.

Density :

The atomic volumes of the transition elements are low compared with the elements of group 1 and 2. This is because the increased nuclear charge is poorly screened by the transition metals are high.

Oxidation states :

Most of transition elements show variable oxidation states. Participation of inner $(n - 1)$ d-electrons in addition to outer ns-electrons because, the energies of the ns and $(n - 1)$ d-subshells are nearly same.

Different oxidation states of first transition series.

| Element | Outer electronic configuration | Oxidation states |
|---------|--------------------------------|--------------------------|
| Sc | $3d^1 4s^2$ | +3 |
| Ti | $3d^2 4s^2$ | +2, +3, +4 |
| V | $3d^3 4s^2$ | +2, +3, +4, +5 |
| Cr | $3d^5 4s^1$ | +2, +3, (+4), (+5), +6 |
| Mn | $3d^5 4s^2$ | +2, +3, +4, (+5), +6, +7 |
| Fe | $3d^6 4s^2$ | +2, +3, (+4), (+5), (+6) |
| Co | $3d^7 4s^2$ | +2, +3, (+4) |
| Ni | $3d^8 4s^2$ | +2, +3, +4 |
| Cu | $3d^{10} 4s^1$ | +1, +2 |
| Zn | $3d^{10} 4s^2$ | +2 |

Characteristics of Oxides and Some Ions of V and Cr

| O.S. | Oxide/ Hydroxide | Behaviour | Ion | Name of Ion | Colour of ion |
|------|--|------------|--------------------------------|---|-------------------|
| +2 | VO | basic | V^{2+} | vanadium (II) (vanadous) | violet |
| +3 | V_2O_5 | basic | V^{3+} | vanadium (III) (vanadic) | green |
| +4 | VO_2 | amphoteric | VO^{2+} $V_2O_9^{2-}$ | oxovanadium (IV) (vanadyl) hypovanadate (vanadite) | blue brown |
| +5 | V_2O_5 | amphoteric | VO_2^+ VO_4^{3-} | dioxovanadium (V) orthovanadate | yellow colourless |
| +2 | CrO $Cr(OH)_2$ | basic | Cr^{2+} | chromium (II) (chromous) | light blue |
| +2 | CrO $Cr(OH)_2$ | basic | Cr^{2+} | chromium (II) (chromous) | light blue |
| +3 | Cr_2O_3 $Cr(OH)_3$ | amphoteric | Cr^{3+} $Cr(OH)$ | chromium (III) chromic chromite | violet green |
| +5 | CrO_3 $CrO_2(OH)_2$ H_2CrO_7 | acidic | CrO_4^{2-} $Cr_2O_7^{2-}$ | chromate dichromate | yellow orange |

Standard electrode potentials :

The value of ionisation enthalpies gives information regarding the thermodynamic stability of the transition metal compounds in different oxidation states. Smaller the ionisation enthalpy of the metal, the stable is its compound.

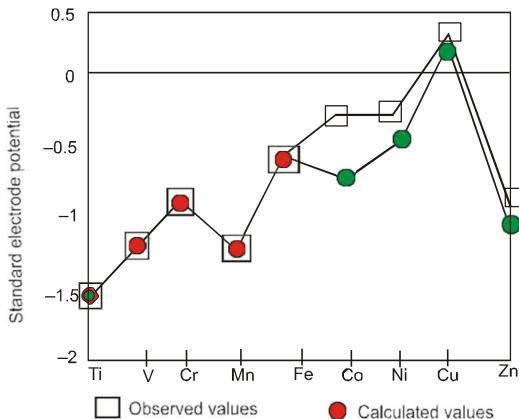
Electrode potentials :

In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration enthalpy, ionisation enthalpy etc. determine the stability of a particular oxidation state in solution.

The overall energy change is

$$\Delta H = \Delta_{\text{sub}} H^\ominus + \text{IE} + \Delta_{\text{hyd}} H$$

The smaller the values of total energy change for a particular oxidation state in aqueous solution, greater will be the stability of that oxidation state. The electrode potentials are a measure of total energy change. Qualitatively, the stability of the transition metal ions in different oxidation states can be determined on the basis of electrode potential data. The lower the electrode potential i.e., more negative the standard reduction potential of the electrode, the more stable is the oxidation state of the transition metal in the aqueous solution.

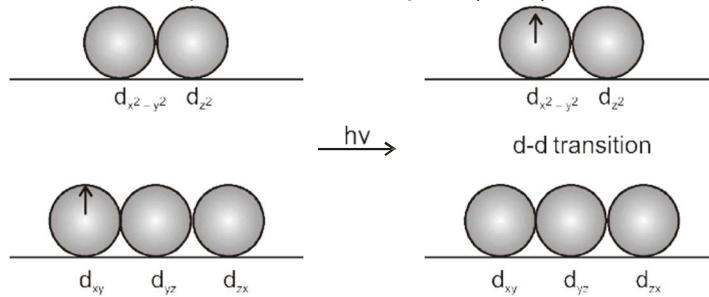


Thermochemical data (kJ mol⁻¹) for the first row Transition Elements and the Standard Electrode potentials for the Reduction of M^{II} to M

| Element (M) | $\Delta_a H^\ominus (M)$ | $\Delta_f H_1^\ominus$ | $\Delta_f H_2^\ominus$ | $\Delta_{hyd} H^\ominus (M^{2+})$ | E^\ominus / V |
|-------------|--------------------------|------------------------|------------------------|-----------------------------------|-----------------|
| Ti | 469 | 661 | 1310 | -1866 | -1.63 |
| V | 515 | 648 | 1370 | -1895 | -1.18 |
| Cr | 398 | 653 | 1590 | -1925 | -0.90 |
| Mn | 279 | 716 | 1510 | -1862 | -1.18 |
| Fe | 418 | 762 | 1560 | -1998 | -0.44 |
| Co | 427 | 757 | 1640 | -2079 | -0.28 |
| Ni | 431 | 736 | 1750 | -2121 | -0.25 |
| Cu | 339 | 745 | 1960 | -2121 | 0.34 |
| Zn | 130 | 908 | 1730 | -2059 | -0.76 |

Formation of Coloured Ions :

Most of the compounds of transition metals are coloured in the solid form or solution form. The colour of the compounds of transition metals may be attributed to the presence of incomplete ($n - 1$) d-subshell.



The excess of other colours constituting white light are transmitted and the compound appears coloured. The observed colour of a substance is always complementary colour of the colour which is absorbed by the substance.

Magnetic Properties :

(i) **Paramagnetic substances :** The substances which are attracted by magnetic field are called paramagnetic substances.

(ii) **Diamagnetic substances :** The substances which are repelled by magnetic field are called diamagnetic substances. The 'spin only' magnetic moment can be calculated from the relation :

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

where n is the number of unpaired electrons and μ is magnetic moment in Bohr magneton (BM) units.

The paramagnetism first increases in any transition series and then decreases. The maximum paramagnetism is observed around the middle of the series (as contains maximum number of unpaired electrons).

Formation of Interstitial Compounds :

Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen.

Catalytic properties :

Many transition metals and their compounds act as good catalysts for various reactions. Of these, the use of Fe, Co, Ni, V, Cr, Mn, Pt, etc. are very common.

(i) The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction.

(ii) In some cases, the transition metal catalysts provide a suitable large surface area for the adsorption of the reactant. This increases the concentration of the reactants at the catalyst surface and also weakens the bonds in the reactant molecules. Consequently, the activation energy gets lowered.

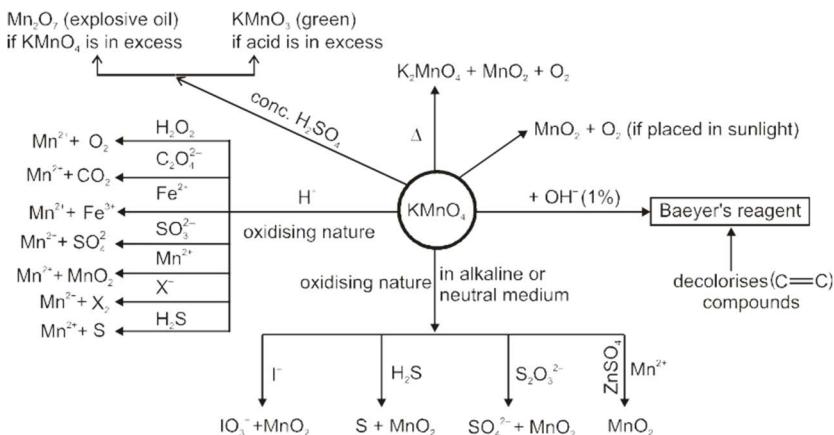
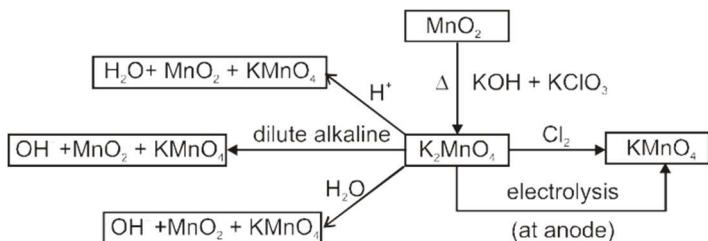
(iii) In some cases, the transition metal ions can change their oxidation states and become more effective as catalysts.

Alloy Formation :

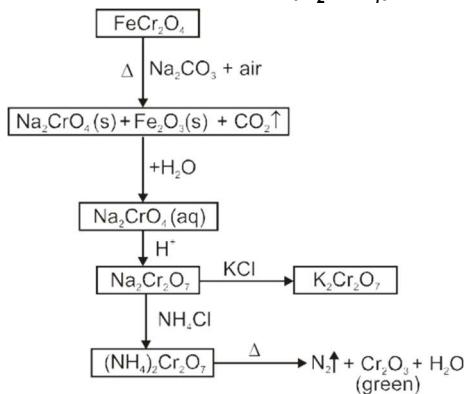
Alloys are hard, have high melting points and are more resistant to corrosion than parent metals.

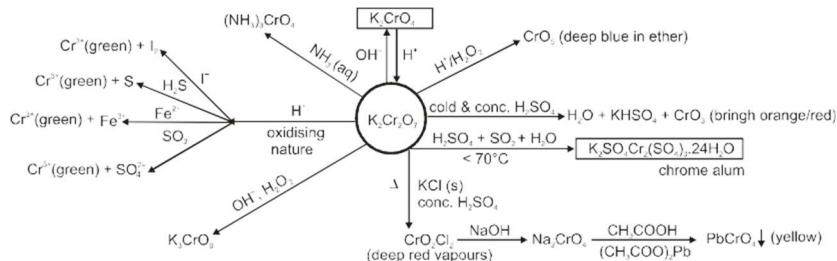
d-BLOCK METAL COMPOUNDS :

1. Potassium permanganate ($KMnO_4$) :



2. Potassium dichromate (K_2CrO_7) :





QUALITATIVE ANALYSIS

Charcoal Cavity Test :

| Observation | | Inference |
|--------------------------------------|---------------------------------|--|
| Incrustation or Residue | Metallic bead | |
| Yellow when hot, white when cold | None | Zn ²⁺ |
| Brown when hot, yellow when cold | Grey bead which marks the paper | Pb ²⁺ |
| No characteristic residue | Red beads or scales | Cu ²⁺ |
| White residue which glows on heating | None | Ba ²⁺ , Ca ²⁺ , Mg ²⁺ |
| Black | None | Nothing definite—generally coloured salt |

Cobalt Nitrate Test :

| S.No. | Metal | Colour of the mass |
|-------|-----------|--------------------|
| 1 | Zinc | Green |
| 2 | Aluminium | Blue |
| 3 | Magnesium | Pink |
| 4 | Tin | Bluish-green |

Flame test :

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

Borax Bead test :

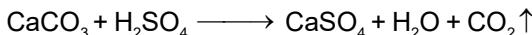
| Metal | Colour in oxidising flame | | Colour in reducing flame | |
|-----------|---------------------------|---------------------|--------------------------|-----------------|
| | When Hot | When Cold | When Hot | When Cold |
| Copper | Green | Blue | Colourless | Brown red |
| Iron | Brown yellow | Pale yellow/Yellow | Bottle green | Bottle green |
| Chromium | Yellow | Green | Green | Green |
| Cobalt | Blue | Blue | Blue | Blue |
| Manganese | Violet/Amethyst | Red/Amethyst | Grey/Colourless | Grey/Colourless |
| Nickel | Violet | Brown/Reddish brown | Grey | Grey |

Analysis of ANIONS (Acidic Radicals) :

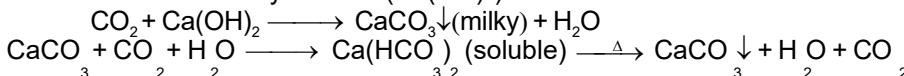
(a) DILUTE SULPHURIC ACID/DILUTE HYDROCHLORIC ACID GROUP:

1. CARBONATE ION (CO_3^{2-}) :

- Dilute H_2SO_4 test : A colourless odourless gas is evolved with brisk effervescence.

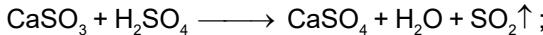


- Lime water/Baryta water ($\text{Ba}(\text{OH})_2$) test :



2. SULPHITE ION (SO_3^{2-}) :

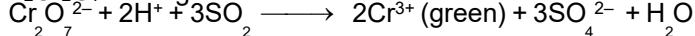
- Dilute H_2SO_4 test :



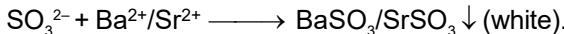
SO_2 has suffocating odour of burning sulphur.

- Acidified potassium dichromate test : The filter paper dipped in acidified

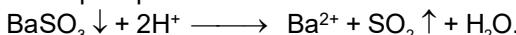
$\text{K}_2\text{Cr}_2\text{O}_7$ turns green.



- Barium chloride/Strontium chloride solution :

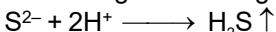


White precipitate dissolves in dilute HCl.

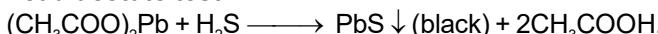


3. SULPHIDE ION (S^{2-}) :

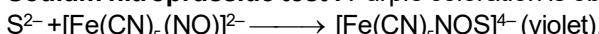
- Dilute H_2SO_4 test : Pungent smelling gas like that of rotten egg is obtained.



- Lead acetate test :



- Sodium nitroprusside test : Purple coloration is obtained.

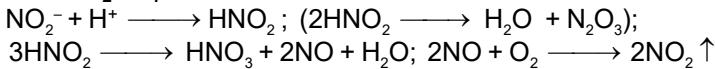


- Cadmium carbonate suspension/ Cadmium acetate solution:

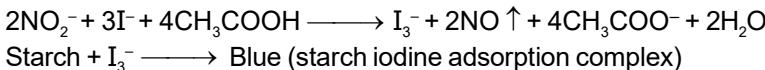


4. NITRITE ION (NO_2O) :

- **Dilute H_2SO_4 test :**



- **Starch iodide test :**

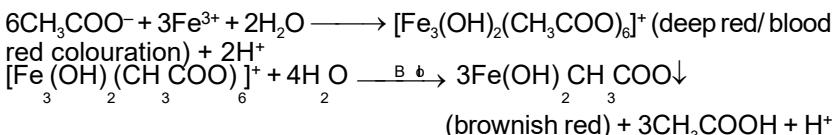


5. ACETATE ION ($\text{CH}_3\text{COO}\text{O}$)

- **Dilute H_2SO_4 test :**



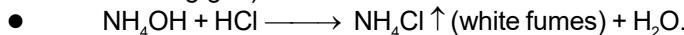
- **Neutral ferric chloride test :**



(b) CONC . H_2SO_4 GROUP :

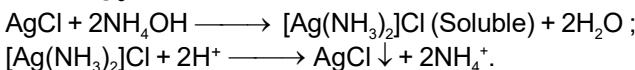
1. CHLORIDE ION (ClO) :

- **Concentrated H_2SO_4 test :** $\text{Cl}^- + \text{H}_2\text{SO}_4 \longrightarrow \text{HCl}$ (colourless pungent smelling gas) + HSO_4^-

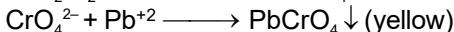
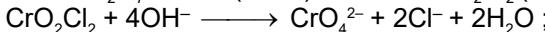


- **Silver nitrate test :** $\text{Cl}^- + \text{Ag}^+ \longrightarrow \text{AgCl} \downarrow \text{ (white)}$

☞ White precipitate is soluble in aqueous ammonia and precipitate reappears with HNO_3 .

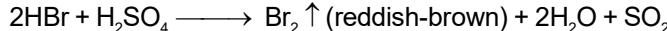


- **Chromyl chloride test :**



2. BROMIDE ION (BrO) :

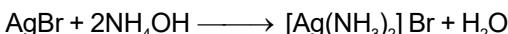
- **Concentrated H_2SO_4 test :**



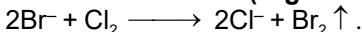
- **Silver nitrate test :**



☞ Yellow precipitate is partially soluble in dilute aqueous ammonia but readily dissolves in concentrated ammonia solution.



- **Chlorine water test (organic layer test) :**



$\text{Br}_2 + \text{CHCl}_3 / \text{CCl}_4 \longrightarrow \text{Br}_2$ dissolve to give reddish brown colour in organic layer.

3. IODIDE ION (I^-) :

- **Concentrated H_2SO_4 test :** $2\text{NaI} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HI}$
 $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 \uparrow$ (pungent smelling dark violet) + $2\text{H}_2\text{O} + \text{SO}_2$

- **Starch paper test :** Iodides are readily oxidised in acid solution to free iodine; the free iodine may then be identified by deep blue colouration produced with starch solution.



- **Silver nitrate test :** Bright yellow precipitate is formed.



☞ Bright yellow precipitate is insoluble in dilute aqueous ammonia but is partially soluble in concentrated ammonia solution.

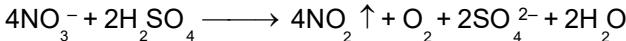
- **Chlorine water test (organic layer test) :**



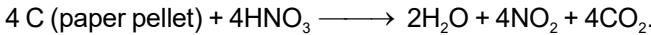
$\text{I}_2 + \text{CHCl}_3 \longrightarrow \text{I}_2$ dissolves to give violet colour in organic layer.

4. NITRATE ION (NO_3^-) :

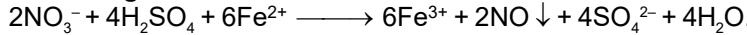
- **Concentrated H_2SO_4 test :** Pungent smelling reddish brown vapours are evolved.



☞ Addition of bright copper turnings or paper pellets intensifies the evolution of reddish brown gas.



- **Brown ring test :**



3. Miscellaneous Group :

1. SULPHATE ION (SO_4^{2-}) :

- **Barium chloride test :**



☞ White precipitate is insoluble in warm dil. HNO_3 as well as HCl but moderately soluble in boiling concentrated hydrochloric acid.

- Lead acetate test ;

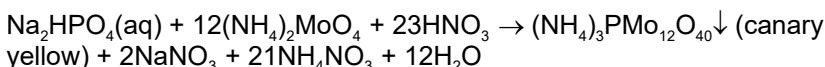


White precipitate soluble in excess of hot ammonium acetate.



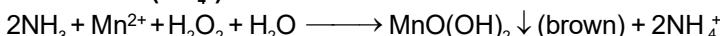
2. PHOSPHATE ION (PO_4^{3-}) :

- Ammonium molybdate test :

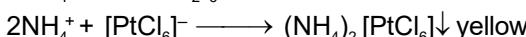
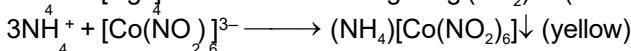


ANALYSIS OF CATIONS

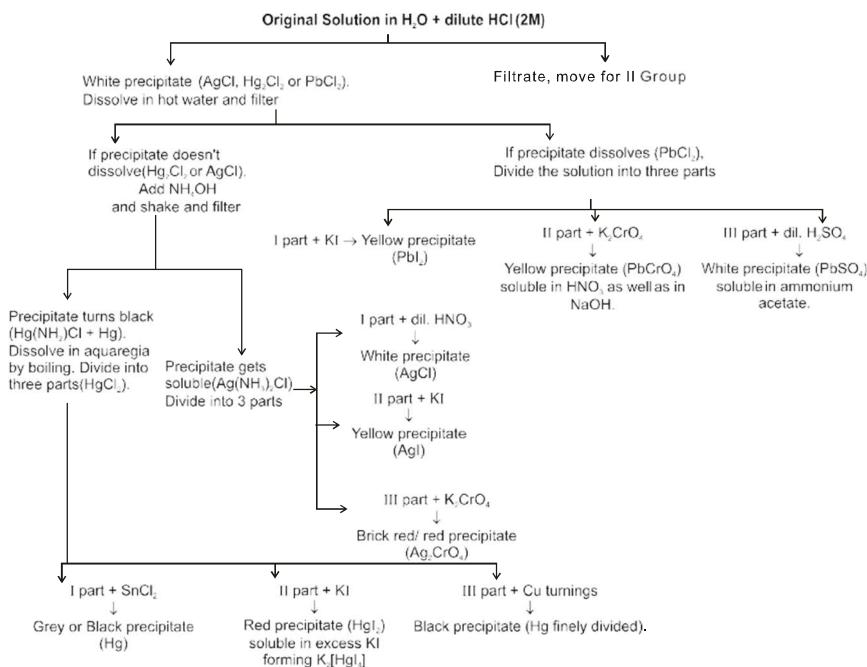
1. AMMONIUM ION (NH_4^+)



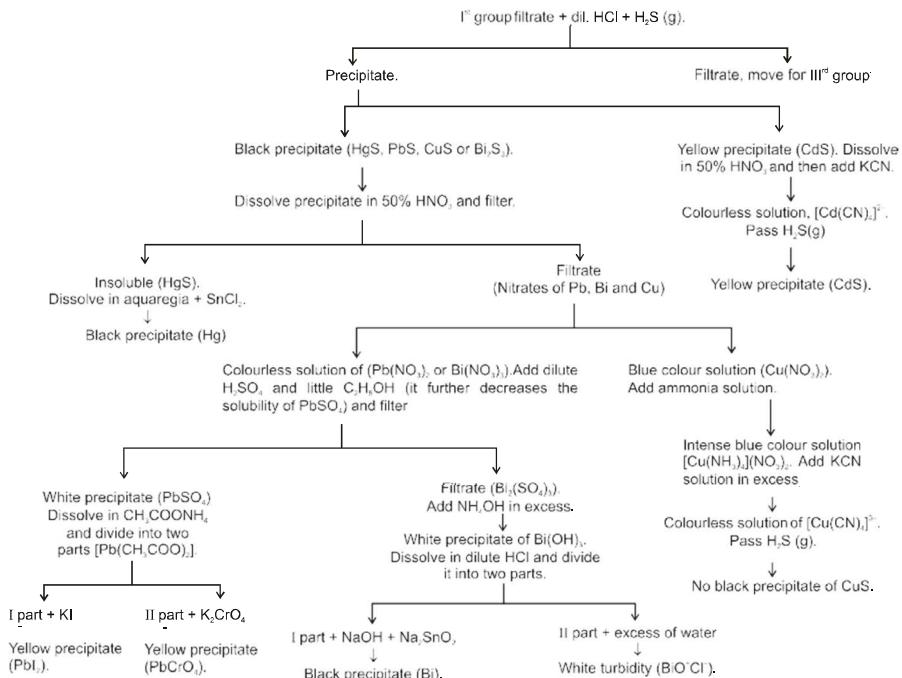
Nessler's reagent (Alkaline solution of potassium tetraiodomercurate(II)) :



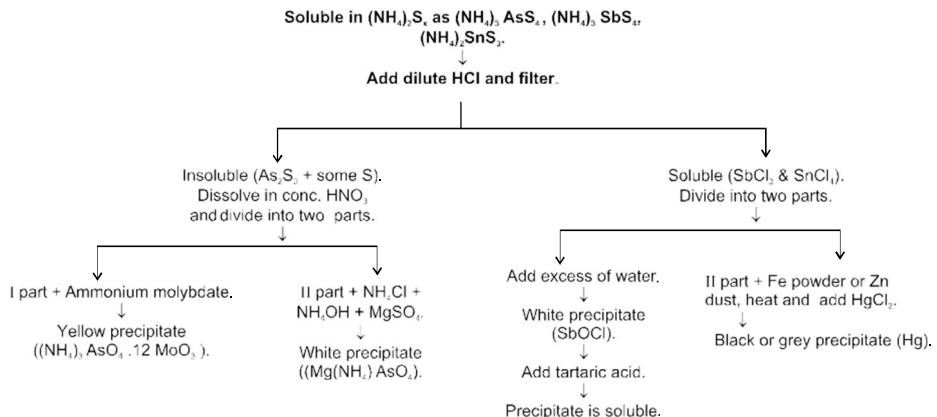
1st GROUP (Pb^{2+} , Hg^{2+} , Ag^+):



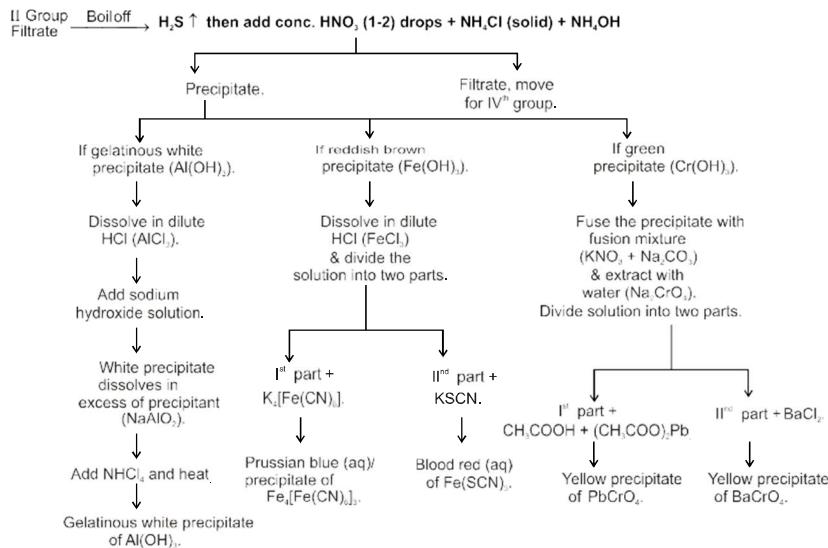
IIA Group (Hg^{2+} , Pb^{2+} , Bi^{3+} , Cu^{2+} , Cd^{2+})



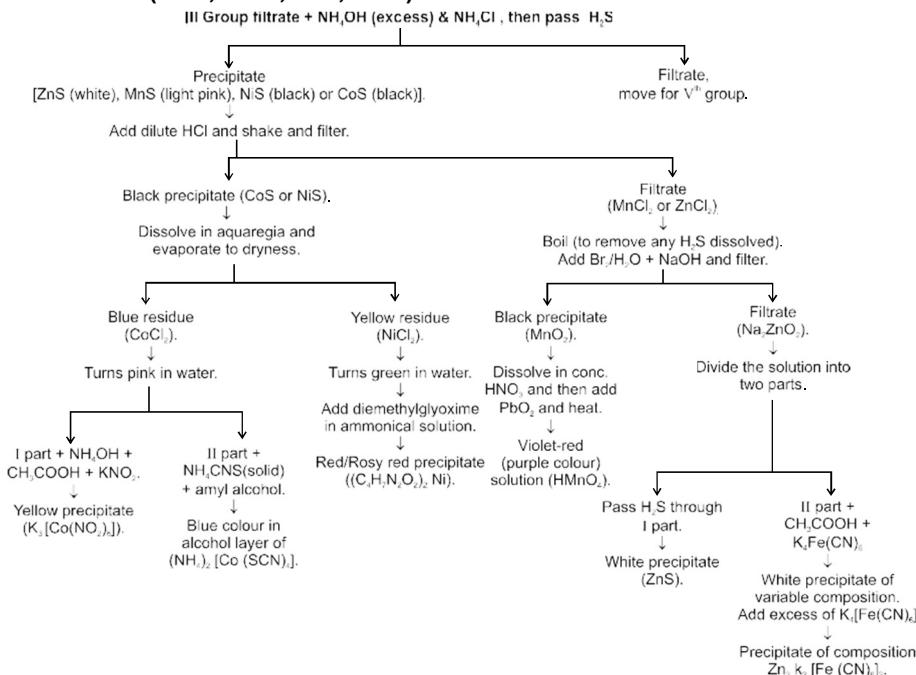
IIIB Group (As^{3+} , Sb^{3+} , Sn^{2+} , Sn^{4+})



IIIrd Group (Al^{+3} , Cr^{+3} , Fe^{+3})



IVth GROUP (Zn^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+}) :



Vth Group (Ba²⁺, Sr²⁺, Ca²⁺) :

IV Group filtrate \longrightarrow Boil off H₂S then add (NH₄)₂CO₃ (aq), NH₄OH & NH₄Cl (s)

White precipitate

(BaCO₃, SrCO₃ or CaCO₃).

Dissolve in CH₃COOH and divide into three parts and test in the sequence given below.

I part + K₂CrO₄.

Yellow precipitate

(BaCrO₄ insoluble in CH₃COOH).

II Part + (NH₄)₂SO₄.

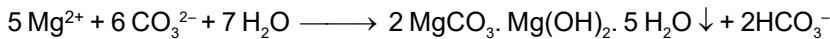
White precipitate

(SrSO₄).

Filtrate,
move for VI group.

VIth GROUP :

MAGNESIUM ION (Mg²⁺) :



Titan Yellow (a water soluble yellow dyestuff) :

It is adsorbed by Mg(OH)₂ producing a deep red colour or precipitate.

ORGANIC CHEMISTRY

• Points to remember in Nomenclature

Examples of Compound containing different functional groups with common / trivial names.

| No. of carbon atoms | Prefix | HCHO (Aldehyde) | HCOOH (Formic acid) | HCOCl (Formyl chloride) | HCONH_2 (Amide) |
|---|---------|---|---|---|--|
| 1 | Form | HCHO Formaldehyde | HCOOH Formic acid | HCOCl Formyl chloride | HCONH_2 Formamide |
| 2 | Acet | CH_3CHO Acetaldehyde | CH_3COOH Acetic acid | CH_3COCl Acetyl chloride | CH_3CONH_2 Acetamide |
| 3 | Propion | $\text{CH}_3\text{CH}_2\text{CHO}$ Propion aldehyde | $\text{CH}_3\text{CH}_2\text{COOH}$ Propionic acid | $\text{CH}_3\text{CH}_2\text{COCl}$ Propionyl chloride | $\text{CH}_3\text{CH}_2\text{CONH}_2$ Propionamide |
| 4 | Butyr | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ n-Butyraldehyde | $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ n-Butyric acid | $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl}$ n-Butyryl chloride | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$ n-Butyramide |
| 5 | Valer | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}$ HO n-Valeraldehyde | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}$ OOH n-Valeric acid | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COCl}$ n-Valeryl chloride | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$ NH ₂ n-Valeramide |
| 3C+1 Double bond | Acryl | $\text{CH}_2=\text{CH-CHO}$ Acrylaldehyde | $\text{CH}_2=\text{CH-COOH}$ Acrylic acid | $\text{CH}_2=\text{CH-COCl}$ Acryl chloride | $\text{CH}_2=\text{CH-CONH}_2$ Acrylamide |
| 4C + 1 Double bond (at 2 nd Carbon. atom) | Croton | $\text{CH}_3-\text{CH}=\text{CH-CHO}$ Crotonaldehyde | $\text{CH}_3\text{CH}_2=\text{CH-COOH}$ Crotonic acid | $\text{CH}_3\text{CH}_2=\text{CH-COCl}$ Crotonyl chloride | $\text{CH}_3\text{CH}_2=\text{CH-CONH}_2$ Crotonamide |

| No. of carbon atoms | Prefix | $-\text{CN}(-\text{O}$ nitrile) | $-\text{N} \rightleftharpoons \text{C}(\text{Oisonitrile})$ If Suffix isocyanide is used than. Carbon atom of – NC not counted. If suffix carbyl amine is used. Carbon atom of – NC not counted. If O-isonitrile is used → Carbon atom of – NC counted | $-\text{COOR}$ Ester |
|--|---------|--|---|--|
| 1 | Form | $\text{H}-\text{C} \equiv \text{N}$ Formonitrile | $\text{H}-\text{N} \rightleftharpoons \text{C}$ Formoisonitrile | HCOOCH_3 Methyl formate |
| 2 | Acet | $\text{CH}_3\text{C} \equiv \text{N}$ Acetonitrile | $\text{CH}_3-\text{N} \rightleftharpoons \text{C}$ Acetoisonitrile | $\text{CH}_3\text{COOCH}_3$ Methyl acetate |
| 3 | Propion | $\text{CH}_3\text{CH}_3 \text{C} \equiv \text{N}$ Propionitrile | $\text{CH}_3\text{CH}_2\text{N} \rightleftharpoons \text{C}$ Propionisonitrile | $\text{CH}_3\text{CH}_2\text{COOCH}_3$ Methyl propionate |
| 4 | Butyr | $\text{CH}_3\text{CH}_2\text{CH}_2 \text{C} \equiv \text{N}$ n-Butyronitrile | $\text{CH}_3\text{CH}_2\text{CH}_2\text{N} \rightleftharpoons \text{C}$ n-Butyroisonitrile | $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$ Methyl n-butyrate |
| 5 | Valer | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \text{C} \equiv \text{N}$ n-Valeronitrile | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N} \rightleftharpoons \text{C}$ n-Valeroisonitrile | $ \begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{COOCH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} $ Methyl isovalerate |
| 3C + 1 Double bond | Acryl | $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{N}$ Acrylonitrile | $\text{CH}_2 = \text{CH}-\text{NC}$ Acrylisonitrile | $\text{CH}_2=\text{CHCOOCH}_3$ Methyl acrylate |
| 4C + 1 Double bond (at 2 nd Carbon. atom) | Croton | $\text{CH}_3\text{CH} = \text{CH} - \text{C} \equiv \text{N}$ Crotononitrile | $\text{CH}_3-\text{CH}=\text{CH}-\text{NC}$ Crotonoisonitrile | $\text{CH}_3\text{CH}=\text{CHCOOCH}_3$ Methyl crotonate |

Secondary suffix of some common functional groups (IUPAC)

A secondary suffix is added to the primary suffix to indicate the nature of the functional group present in the organic compounds. Secondary suffix of important functional groups are given below in their decreasing order of seniority.

| Class | Name | Suffix | Prefix |
|----------------------------|----------------------|---------------------------------------|---------------------------------|
| 1. R-COOH | Alkanoic Acid | -oic acid (carboxylic acid) | carboxy |
| 2. R-SO ₃ H | Alkane sulhonic Acid | -sulphonic acid | sulpho |
| 3. R-C(=O)-C(=O)-R | Alkanonic Anhydride | -oic anhydride (carboxylic anhydride) | ----- |
| 4. R-COO ⁺ R | Alkyl alkanoate | -oate (carboxylate) | alkoxy carbonyl or alkanoyl oxy |
| 5. R-C(=O)-X | Alkanoyl halide | -oyl halide (carbonyl halide) | halo carbonyl |
| 6. R-C(=O)-NH ₂ | Alkanamide | -amide (carboxamide) | carbamoyl |
| 7. R-C≡N | Alkanenitrile | -nitrile (carbonitrile) | cyano |
| 8. R-C(=O)-H | Alkanal | -al (carbaldehyde) | formyl / oxo |
| 9. R-C(=O)-R | Alkanone | -one | oxo |
| 10. R-OH | Alkanol | -ol | hydroxy |
| 11. R-SH | Alkanethiol | -thiol | mercapto |
| 12. R-NH ₂ | Alkanamine | -amine | amino |

IUPAC system of nomenclature

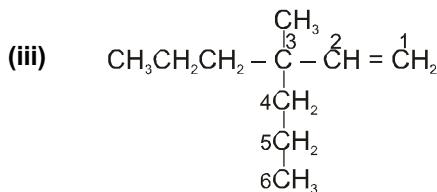
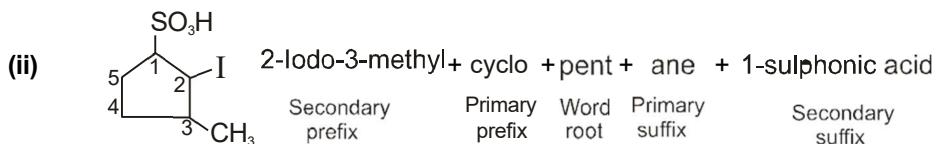
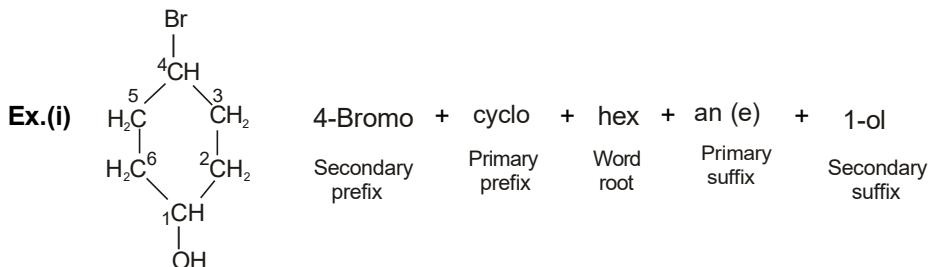
The IUPAC name of any organic compound consists of maximum five parts in the following sequence.

Secondary prefix + Primary prefix + Word root + Primary suffix + Secondary suffix

The following examples illustrate the use of word root, primary suffix and secondary suffix in naming of organic compounds.

| Organic compounds | Word root | Primary suffix | Secondary suffix | IUPAC name |
|---|-----------|----------------|------------------|----------------|
| CH ₃ CH ₂ OH | Eth | an(e) | ol | Ethanol |
| CH ₃ CH ₂ CH ₂ NH ₂ | Prop | an(e) | amine | Propanamine |
| CH ₃ CH ₂ CH ₂ COOH | But | an(e) | oic acid | Butanoic acid |
| CH ₃ CH ₂ CN | Prop | an(e) | nitrile | Propanenitrile |
| CH ₂ = CHCHO | Prop | en(e) | al | Propenal |
| HC ≡ CCOOH | Prop | yn(e) | oic acid | Propynoic acid |

The following examples illustrate the use of word root , primary prefix and secondary prefix in naming of organic compounds.



Position of double bond will be indicated as no. 1, Hence name will be 3–Methyl–3–propylhex–1–ene

Common and IUPAC Names of Some Organic Compounds

| S.No. | Compound | Common names | IUPAC name |
|-------|---|-------------------|--------------------------|
| 1. | $\text{CH}_3\text{CH}=\text{CH}_2$ | Propylene | Propene |
| 2. | $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} = \text{CH}_2 \\ \diagup \\ \text{CH}_3 \end{array}$ | Isobutylene | 2-Methylpropene |
| 3. | $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C} \equiv \text{CH} \end{array}$ | Methyl acetylene | Propyne |
| 4. | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{Cl} \end{array}$ | Isobutyl chloride | 1-Chloro-2-methylpropane |

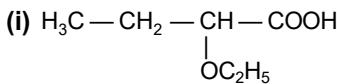
| | | | |
|-----|--|--|---------------------------|
| 5. | $ \begin{array}{c} \text{CH}_2 - \text{Br} \\ \\ \text{CH}_2 - \text{Br} \end{array} $ | Ethylene dibromide | 1, 2-Dibromoethane |
| 6. | $\text{CH}_2 = \text{CH} - \text{Cl}$ | Vinyl chloride | Chloroethene |
| 7. | $ \begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{OH} \end{array} $ | Isopropyl alcohol | Propan-2-ol |
| 8. | $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{OH}$ | Allyl alcohol | Prop-2-en-1-ol |
| 9. | $ \begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array} $ | Glycerol or Glycerine | Propane-1, 2, 3-triol |
| 10. | $\text{CH}_3 - \text{CHO}$ | Acetaldehyde | Ethanal |
| 11. | $\text{CH}_3 - \text{CO} - \text{CH}_2\text{CH}_3$ | Ethyl methyl ketone | Butanone |
| 12. | $\text{CH}_3 - \text{COOH}$ | Acetic acid | Ethanoic acid |
| 13. | $ \begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array} $ | Oxalic acid | Ethanedioic acid |
| 14. | $ \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} - \text{C} - \text{COOH} \end{array} $ | Pyruvic acid | 2-Oxopropanoic acid |
| 15. | $\text{CH}_3 - \text{COCl}$ | Acetyl chloride | Ethanoyl chloride |
| 16. | $\text{CH}_3 - \text{CONH}_2$ | Acetamide | Ethanamide |
| 17. | $\text{CH}_3 - \text{NH}_2$ | Methylamine | Methanamine |
| 18. | $\text{CH}_3 - \text{CN}$ | Methyl cyanide or Acetonitril | Ethanenitrile |
| 19. | $\text{CH}_3 - \text{N}^+ = \text{C} \text{O}$ | Methyl isocyanide or Methyl carbylamine | Methane isocyanide |
| 20. |  | Toluene | Methylbenzene or Toluene● |

• Points to remember in Structure Isomerism

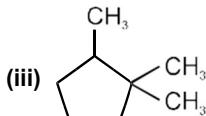
| Isomers | Characteristics | Conditions |
|------------------------|---|--|
| (1) Chain Isomers | They have different size of main chain or side chain | They have same nature of locants |
| (2) Positional Isomers | They have different position of locants | They should have same size of main chain and side chain and same nature of locant |
| (3) Functional Isomers | Different nature of locant | Chain and positional isomerism is not considered |
| (4) Metamerism | Different nature of alkyl group along a polyvalent functional group | They should have same nature of functional groups chain & positional isomer is ignored |
| (5) Tautomerism | Different position of hydrogen atoms | The two functional isomers remains in dynamic equilibrium to each other |

MISCELLANEOUS SOLVED PROBLEMS

1. Write the IUPAC name of following compounds.

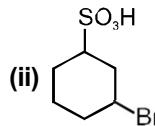


(ii) 3-Bromocyclohexane-1-sulphonic acid

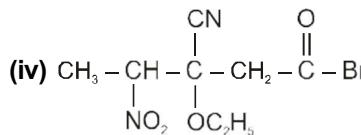


(iv) 3-Cyano-3-ethoxy-4-nitropentanoyl bromide

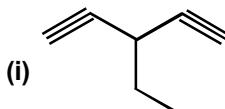
Sol. (i) 2-Ethoxybutanoic acid



(iii) 1,1,2-Trimethylcyclopentane

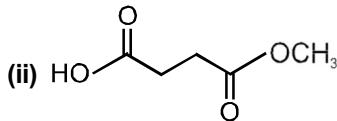


2. Draw the structure of following IUPAC name.



(ii) 3-Methoxycarbonylpropanoic acid

Sol. (i) 3-Ethylpenta-1,4-diyne



3. Find total number of structure isomers of dimethyl cyclopropane and dimethyl cyclobutane are respectively.

(A) 4, 6

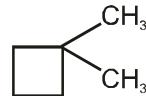
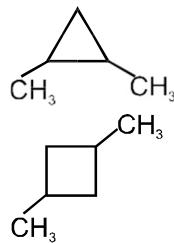
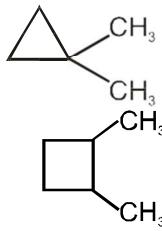
(B) 3, 4

(C) 4, 5

(D) 2, 3

Ans. (D)

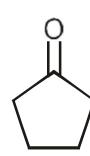
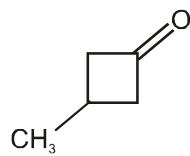
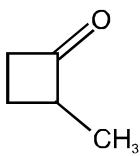
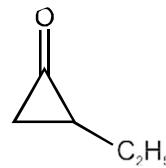
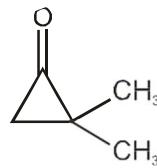
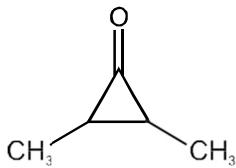
Sol.



4. How many structures of cycloalkanone are possible with molecular formula C_5H_8O .

Ans. 6

Sol.

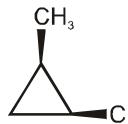
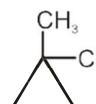
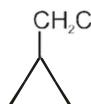


5. Find out the total number of cyclic isomers of the compound (X) C_4H_7Cl .

Ans. 4.

Sol. $X = C_4H_7Cl$

$$DU = 5 - \frac{8}{2} = 1$$



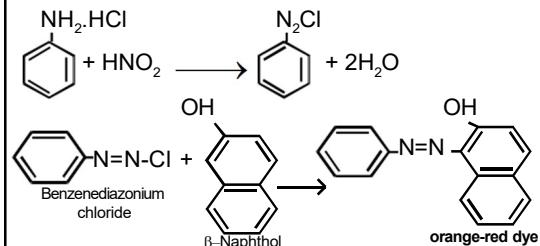
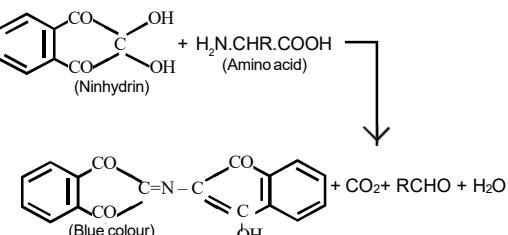
Total = 4

Identification of Functional Groups by Laboratory Tests

| Functional Groups | Reagent | Observation | Reaction | Remarks |
|---------------------------------|---|--|---|--|
| C—C (Alkane) | conc. H_2SO_4 conc. NaOH KMnO_4 LiAlH_4 | NR NR NR NR | ----- | Inert paraffins |
| C=C / C≡C | [Bayer's reagent] alk. dil. cold KMnO_4 | Pink colour disappears | $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{alk. KMnO}_4} \text{CH}_2\begin{matrix} \\ \text{OH} \end{matrix} - \text{CH}_2\begin{matrix} \\ \text{OH} \end{matrix}$ | Hydroxylation |
| C=C / C≡C C=C C≡C | $\text{Br}_2 / \text{H}_2\text{O}$ O_3 (ozone) O_3 | Red colour decolourises >C=O Compounds Acid formed. | $\text{Br}_2 + \text{CH}_2=\text{CH}_2 \longrightarrow \text{white ppt}$ $\text{H}_2\text{C}=\text{CH}_2 + \text{O}_3 \xrightarrow{\text{Zn/H}_2\text{O}} 2\text{HCHO}$ $\text{R}-\text{C}\equiv\text{C}-\text{R}' \xrightarrow{\text{O}_3} \text{RCOOH} + \text{R}'\text{COOH}$ | Bromination Ozonolysis Ozonolysis |
| R—C≡CH (Terminal alkyne) | (a) Cuprous chloride+ NH_4OH (b) $\text{AgNO}_3 + \text{NH}_4\text{OH}$ | Red ppt. White ppt. | $\text{R}-\text{C}\equiv\text{CH} + \text{CuCl} \xrightarrow{\text{NH}_4\text{OH}} \text{R}-\text{C}\equiv\text{C} \text{ Cu} \downarrow \text{ (red)}$ $\text{R}-\text{C}\equiv\text{CH} + \text{Ag}^+ \longrightarrow \text{R}-\text{C}\equiv\text{C} \text{ Ag} \downarrow \text{ (white)}$ | |
| (R—OH) ROH 3° 2° 1° | Na Lucas Reagent [Conc. HCl + anhyd. ZnCl_2] | Bubbles of H_2 come out (3°) Cloudiness appears immediately (2°) Cloudiness appears within 5 min. (1°) Cloudiness appear after 30 min. | $2\text{ROH} + \text{Na} \rightarrow 2\text{RONa} + \text{H}_2 \uparrow$ $\text{R}-\text{OH} + \text{HCl} \xrightarrow{\text{anhydrous ZnCl}_2} \text{R}-\text{Cl} + \text{H}_2\text{O}$ cloudiness | Presence of active 'H' Lucas Test I. ter.alcohol II. sec. alcohol III. pri.alcohol |

| Functional Groups | Reagent | Observation | Reaction | Remarks |
|--|---|--|--|-------------------------|
| Ar-OH Enols | FeCl ₃ (Neutral) | Coloured ppt. (violet, blue, green buff) | $6\text{C}_6\text{H}_5\text{OH} + \text{FeCl}_3 \longrightarrow [\text{Fe}(\text{PhO})_6]^{3-}$ | Test of enols/phenols |
| >C=O | 2, 4-Dinitrophenyl hydrazine (2, 4-DNP) solution | Yellow orange ppt. | $\text{>C=O} + \text{H}_2\text{N-NH-} \begin{array}{c} \text{NO}_2 \\ \\ \text{C}_6\text{H}_3\text{NO}_2 \\ \\ \text{NO}_2 \end{array}$ $\text{>C=N-NH-} \begin{array}{c} \text{NO}_2 \\ \\ \text{C}_6\text{H}_3\text{NO}_2 \\ \\ \text{NO}_2 \end{array} \downarrow \text{(yellow orange ppt.)}$ | DNP-test |
| R-CHO | Fehling solution A & B | Red ppt. | $\text{RCHO} + \text{Cu}^{+2} \rightarrow \text{RCOOH} + \text{Cu}_2\text{O} \downarrow + 2\text{H}_2\text{O}$ Fehling sol ^l . Red | Fehling's test |
| | Tollen's reagent | Black ppt. or silver mirror | $\text{RCHO} + \text{Ag}^+ \rightarrow \text{RCOOH} + 2\text{Ag} \text{ (Silver mirror)}$ | Tollen's test |
| | Schiff's Reagent * | Pink colour resume | | |
| R-COCH ₃ or ArCOCH ₃ or CH ₃ CHO | I ₂ / NaOH | Yellow ppt of CHI ₃ (iodoform) | $\text{R}-\text{C}(=\text{O})-\text{CH}_3 \xrightarrow{\text{I}_2 / \text{NaOH}} \text{R}-\text{C}(=\text{O})-\text{ONa} + \text{CHI}_3$ (Iodoform) | Iodoform reaction |
| $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{math}$ | Blue litmus | Litmus change to red. | | Litmus test. |
| | Conc. NaHCO ₃ solution | Effervescence evolve. | $\text{R}-\text{COOH} + \text{NaHCO}_3 \longrightarrow \text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ | Sodium bicarbonate test |
| Ester | NaOH, phenolphthalein | Pink colour \downarrow disappear on heating. | $\text{RCOOR}' + \text{NaOH} + \text{Phenolphthalein} \xrightarrow{\Delta} \text{RCOOH} + \text{R}'\text{OH}$ (Colourless solution) (pink) | |
| Amides | Conc. NaOH, Δ | Smell of NH ₃ | $\text{RCONH}_2 + \text{NaOH} \xrightarrow{\Delta} \text{RCOONa} + \text{NH}_3 \uparrow$ | |

* Schiff's reagent : p-Rosaniline hydrochloride saturated with SO₂ so it is colourless. The pink colour is resumed by RCH=O.

| Functional Groups | Reagent | Observation | Reaction | Remarks |
|--|---|--|---|----------------------|
| Nitro Compounds (RCH_2NO_2) or ArNO_2 | Mulliken's test | black ppt | $\text{Ar}-\text{NO}_2 \xrightarrow[\substack{(1) \\ (\text{R}-\text{NO}_2)}]{\text{Zn / NH}_4\text{Cl, } \Delta} \text{ArNHOH} \xrightarrow[\substack{(2) \\ \text{AgNO}_3 + \text{NH}_4\text{OH}}]{\text{Ag}} \text{Ag} \downarrow$ | |
| Amines(pri.) RNH_2 | $\text{CHCl}_3, \text{KOH}$ | Nauseating odour (Offensive smell) (Carbylamine) | $\text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{RNC} + 3\text{KCl} + 3\text{H}_2\text{O}$ | Carbylamine Reaction |
| | HNO_2 ($\text{NaNO}_2 + \text{HCl}$) | Effervescence of N_2 | $\text{RNH}_2 + \text{HONO} \rightarrow \text{ROH} + \text{N}_2 + \text{H}_2\text{O}$ | |
| Ar. amines. ArNH_2 | HNO_2 ($\text{NaNO}_2 + \text{HCl}$) + β -Naphthol | Orange red dye is formed | $\text{NaNO}_2 + \text{HCl} \rightarrow \text{NaCl} + \text{HNO}_2$ $\text{NH}_2\text{HCl} + \text{HNO}_2 \rightarrow \text{N}_2\text{Cl} + 2\text{H}_2\text{O}$  | Azo dye test |
| R_2NH Sec. Amines | (i) $\text{NaNO}_2 + \text{H}_2\text{SO}_4$ (ii) Phenol | red colouration Liebermann test |  | Ninhydrin test |
| Carbohydrate | Molisch's reagent (10% α -naphthol in alcohol). | Violet colour | | |
| Amino acids | Ninhydrin reagent (0.2 % sol.) | Blue colour | | |

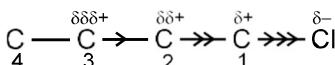
• Points to remember in General Organic Chemistry

1. Inductive effect

The normal C–C bond has no polarity as two atoms of same electronegativity (EN) value are connected to each other. Hence the bond is nonpolar. Consider a carbon chain in 1-Chloro butane, here due to more EN of Cl atom C–Cl bond pair is slightly displaced towards Cl atom hence creating partial negative (δ^-) charge over Cl atom and partial positive (δ^+) charge over C₁ atom.

Now since C₁ is slightly positive, it will also cause shifting of C₁–C₂ bond pair electrons towards itself causing C₂ to acquire small positive charge. Similarly C₃ acquires slightly positive charge creating an induction of charge in carbon chain. Such an effect is called inductive effect.

Diagram showing I effect



The arrow shows electron withdrawing nature of – Cl group.

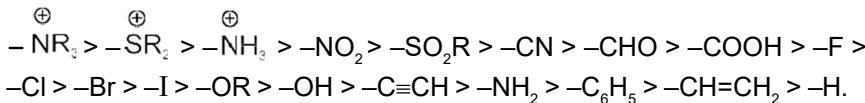
Thus inductive effect may be defined as a permanent displacement of σ bond pair electrons due to a dipole. (Polar bond)

Some important points are:

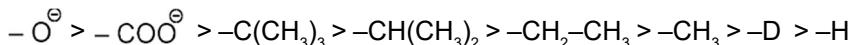
- It can also be defined as polarisation of one bond caused by polarisation of adjacent bond.
- It is also called transmission effect.
- It causes permanent polarisation in molecule, hence it is a permanent effect.
- The displacement of electrons takes place due to difference in electronegativity of the two atoms involved in the covalent bond.
- The electrons never leave their original atomic orbital.
- Its magnitude decreases with distance and it is almost negligible after 3rd carbon atom.
- The inductive effect is always operative through σ bond, does not involve π bond electron.

Types of inductive effects :

(a) -I Effect : The group which withdraws electron cloud is known as -I group and its effect is called -I effect. Various groups are listed in their decreasing -I strength as follows.

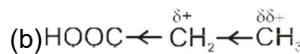
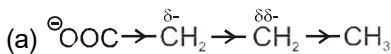


(b) +I effect : The group which releases electron cloud is known as +I group and effect is +I effect.



The hydrogen atom is reference for + I and - I series. The inductive effect of hydrogen is assumed to be zero.

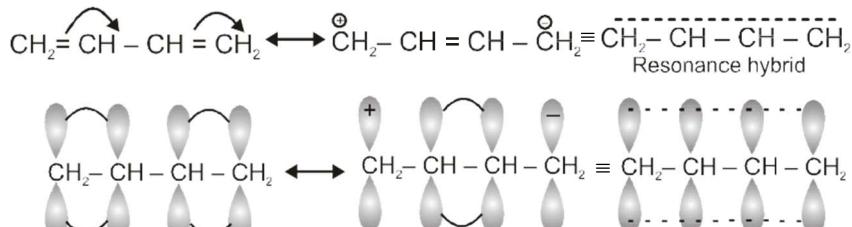
Ex. Let us consider effect of COOH & - COO⁻ in carbon chain



Due to $\text{e}\emptyset$ donating nature of $-\text{COO}^\ominus$ carbon chain has become partially negative but $-\text{COOH}$ is - I group therefore carbon chain has become partially positive.

2. Resonance

Resonance is the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular species, all those possible structures are known as resonating structures or canonical structures. Resonating structures are only hypothetical but they all contribute to a real structure which is called resonance hybrid. The resonance hybrid is more stable than any resonating structure.



Resonance hybrid :

The most stable resonating structure contribute maximum to the resonance hybrid and less stable resonating structure contribute minimum to resonance hybrid.

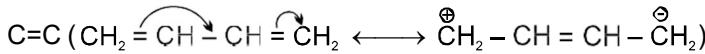
Conjugation:

A given atom or group is said to be in conjugation with an unsaturated system if:-

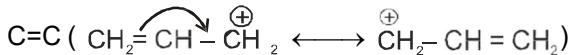
- (i) It is directly linked to one of the atoms of the multiple bond through a single bond.
- (ii) It has bond, positive charge, negative charge, odd electron or lone pair electron.

Types of Conjugation :

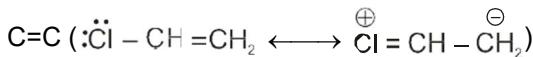
1. Conjugation between C = C and



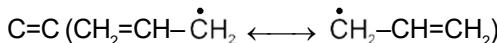
2. Conjugation between +ve charge and



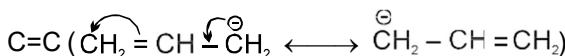
3. Conjugation between lone pair and



4. Conjugation between odd electron and

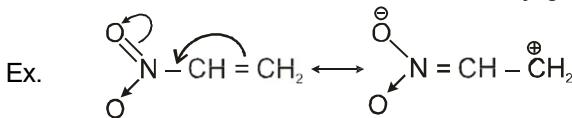


5. Conjugation between negative charge and



3. Mesomeric effect (or Resonance effect)

Mesomeric effect is defined as permanent effect of π electron shifting from multiple bond to atom or from multiple bond to single bond or from lone pair to single bond. This effect mainly operates in conjugated system of double bond. So that this effect is also known as conjugate effect.

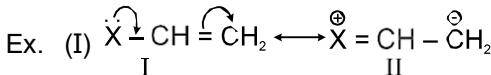
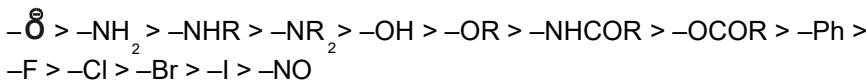


Types of Mesomeric effects :

(a) Positive Mesomeric effect (+M effect) :

When the group donates electron to the conjugated system it shows + M effect.

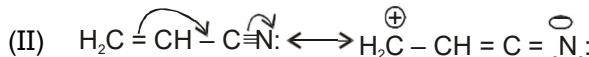
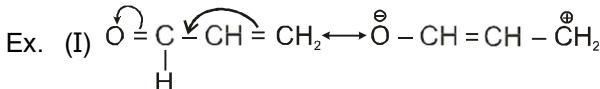
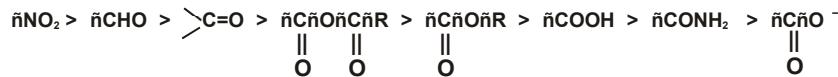
Relative order of +M groups (usually followed) :



(b) Negative Mesomeric effect (nM effect) :

When the group withdraws electron from the conjugated system, it shows – M effect

Relative order of –M groups (usually followed) :

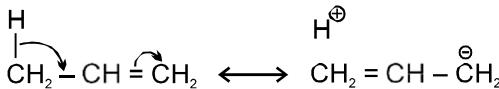


4. Hyperconjugation

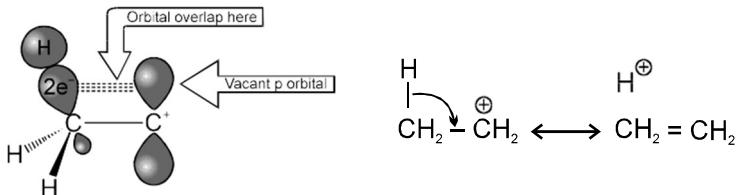
It is delocalisation of sigma electron with p-orbital. Also known as $\sigma \pi$ -conjugation or no bond resonance. It may take place in alkene, alkynes, carbocation, free radical, benzene nucleus.

Necessary Condition : Presence of at least one hydrogen at saturated carbon which is α with respect to alkene, alkynes, carbocation, free radical, benzene nucleus.

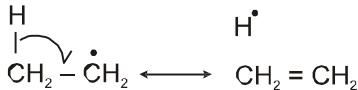
(i) Hyperconjugation in alkene



(ii) Hyperconjugation in carbocation



(iii) Hyperconjugation in radical

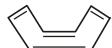


5. Aromatic character [The Huckel 4n + 2 rule]

The following rules are useful in predicting whether a particular compound is aromatic or non-aromatic. Aromatic compounds are cyclic and planar. Each atom in an aromatic ring is sp^2 hybridised. The cyclic π molecular orbital (formed by overlap of p-orbitals) must contain $(4n + 2) \pi$ electrons, i.e., 2, 6, 10, 14 π electrons. Where $n =$ an integer 0, 1, 2, 3,.....

Aromatic compounds have characteristic smell, have extra stability and burn with sooty flame.

Comparision between aromatic, anti aromatic and non-aromatic compounds.

| Characteristics | Aromatic compounds (A) | Anti Aromatic compounds (B) | Non-Aromatic compounds (C) |
|-----------------------------------|---|---|---|
| Example |  |  |  |
| 1. Structure | Cyclic, planar all atoms of ring sp^2 hybridised | Cyclic, planar all atoms of ring sp^2 hybridised | Cyclic or acyclic planar, or non planar sp or sp^2 or sp^3 |
| 2. No. of πe^- s in the ring | $(4n+2)\pi e^-$ (Huckel's rule) | $(4n)\pi e^-$ | Any no. of πe^- s |
| 3. MOT | Unpaired $e\delta$ s in B.M.O. | Some πe^- s in non-bonding M.O. | B.M.O. / Non-bonding M.O. |
| 4. Overlapping | Favourable over lapping of p orbital | Unfavourable over lapping of p orbital | Simple overlapping like alkenes |
| 5. Resonance energy (R.E.) | Very high R.E. $> 20-25$ kcal/mol | Zero | 4-8 kcal/mol like alkenes |
| 6. Stability | Have extra stability due to close conjugation of πe^- s | Unstable not-exist at room temperature | Normal stability like a conjugated system |
| 7. Characteristic Reactions | Electrophilic substitution Reaction | Dimerisation reaction to attain stability | Electrophilic addition reaction like alkenes |

Stability of compounds : Aromatic > Non-Aromatic > Anti-Aromatic

(A) Carbocation :

Definition : A carbon intermediate which contain three bond pair & a positive charge on it is called carbocation.

Hybridisation : Carbocation may be sp^2 & sp hybridised

Hybridisation

sp^2

Example

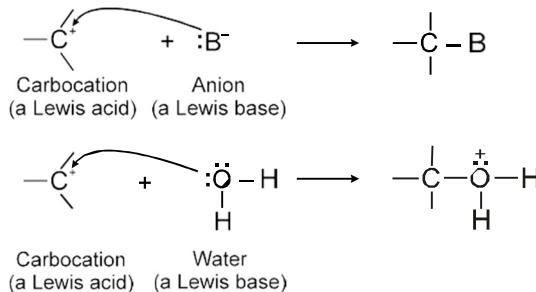


sp



Carbocations are electron deficient. They have only six electrons in their valence shell, and because of this, carbocations act as Lewis acids. Most of the carbocations are short-lived and highly reactive, they occur as intermediates

in some organic reactions. Carbocations react with Lewis bases or ions that can donate the electron pair, that they need to achieve a stable octet of electrons (i.e., the electronic configuration of a noble gas):

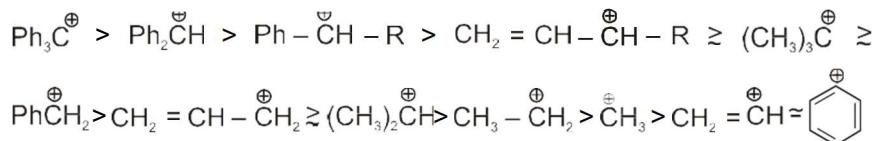


Because carbocations are electron seeking reagents, chemists call them electrophiles. All Lewis acids, including protons, are electrophiles. By accepting an electron pair, a proton achieves the valence shell configuration of helium; carbocations achieve the valence shell configuration of neon.

Stability : Carbocations are stabilised by

| | |
|--|--|
| (i) + I effect (iii) Hyperconjugation | (ii) + M effect (iv) delocalisation of charge |
|--|--|

General stability order :



(B) Carbanion :

Definition: A carbon intermediate which contains three bond pairs and a negative charge on it, is called carbanion.

Hybridisation : Hybridisation of carbanion may be sp^3 , sp^2 & sp .

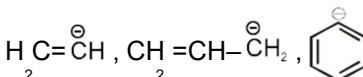
Hybridisation

Example

sp³



sp²



sp

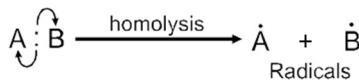


Stability of carbanion : Carbanions are stabilised by electron withdrawing effect as

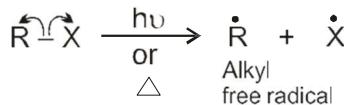
(i) – I effect (ii) – m effect (iii) Delocalisation of charge

(C) Free Radicals :

Homolysis of covalent bond results into free radical intermediates possess the unpaired electrons.



It is generated in presence of Sun light, Peroxides or High temperature



Free Radical : An uncharged intermediate which has three bond pair and an unpaired electron on carbon.

Note : (i) It is Neutral species with odd $e\emptyset$

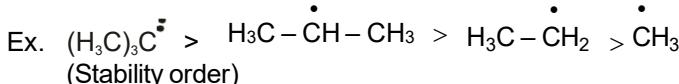
(ii) It is paramagnetic in nature due to odd $e\emptyset$

(iii) No rearrangement is observed generally.

(iv) Carbon atom having odd electron is in sp^2 hybridised state

(v) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature it generally proceeds via free radical intermediate.

☞ **Stability of free radical :** It is stabilised by resonance, hyperconjugation and + I groups.



(D) Carbenes (Divalent Carbon intermediates) :

Definition : There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon species are called carbenes. Most carbenes are highly unstable that are capable of only fleeting existence. Soon after carbenes are formed, they usually react with another molecules.

Methods of preparation of carbene :



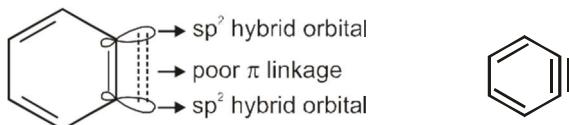
(E) Nitrenes :

The nitrogen analog of carbenes are nitrenes. They are very much reactive since in them octet of N is incomplete. In nitrenes only one valencies of N are satisfied.



(F) Benzyne :

The benzene ring has one extra C – C π bond in benzyne

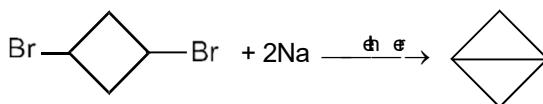
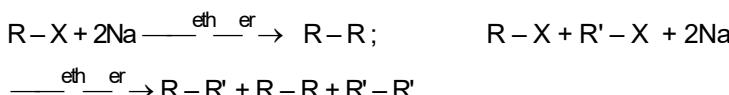


Clearly, we can see that the newly formed π bond cannot enter in resonance with other π orbitals of ring. since it is in perpendicular plane.

It is also important to note that hybridisation of each carbon involved in 'Benzynic bond' is sp^2 since the overlap between these sp^2 hybrid orbitals is not so much effective.

• Points to remember in Alkane

Wurtz reaction (Reagent : Na, ether) 1U & 2U alkyl halides give this reaction.

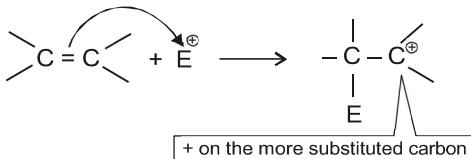


• Points to remember in Alkene & Alkyne

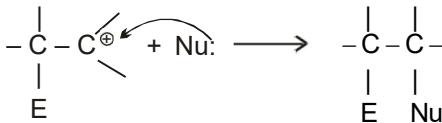
Characteristic reaction of Alkene & Alkyne is Electrophilic addition reaction.

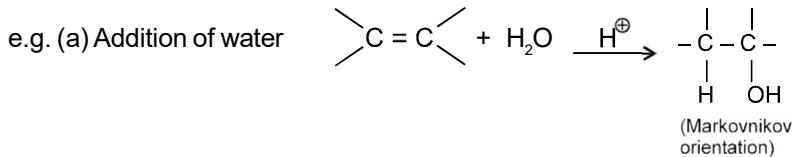
Mechanism

Step 1 : Attack of the electrophile on π bond forms a carbocation.

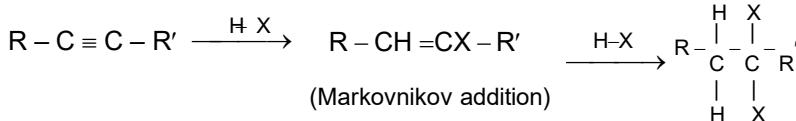


Step 2 : Attack by a nucleophile gives the product of addition.





(b) Addition of hydrogen halides (where $\text{HX} = \text{HCl}, \text{HBr}, \text{HI}$)



Note: When electrophiles are: $\text{Cl}^+, \text{Br}^+, \text{I}^+, \text{NO}_2^+$ or Hg^{2+} then stereochemistry is important and major product is formed by anti addition.

• Points to remember in Alkyl halide

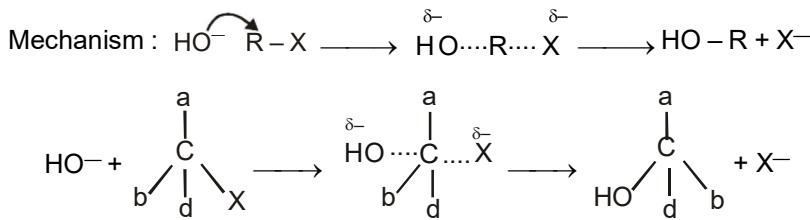
Nucleophilic substitution Reaction ($\text{S}_{\text{N}}1, \text{S}_{\text{N}}2$)

$\text{S}_{\text{N}}1$ reaction :



Alkylhalide are hydrolysed to alcohol very slowly by water, but rapidly by silver oxide suspended in boiling water.

$\text{S}_{\text{N}}2$ reaction :



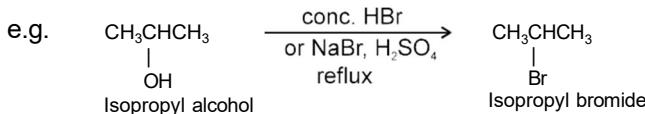
• Points to remember in Alcohol

$\text{S}_{\text{N}}1$ reaction :

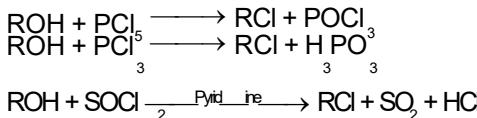


Reactivity of HX : $\text{HI} > \text{HBr} > \text{HCl}$

Reactivity of ROH : allyl, benzyl $> 3\text{B} > 2\text{B} > 1\text{B}$ (Carboocation)



S_N2 reaction :



Williamson's synthesis :

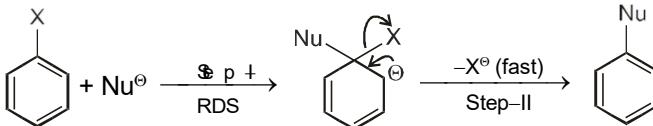
It is the reaction in which sodium or potassium alkoxide is heated with an alkyl halide (S_N2).



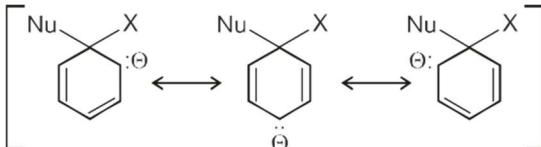
This method is particularly useful for preparing mixed ethers.

Nucleophilic Aromatic Substitution of aryl halides (S_N2Ar):

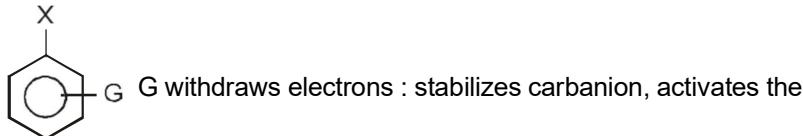
- An electron withdrawing group at ortho or para positions with respect to a good leaving group are necessary conditions for S_N2Ar.



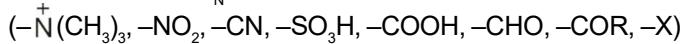
Intermediate ion is stabilized by resonance, and are stable salts called Meisenheimer salts.



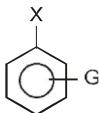
- A group that withdraws electrons tends to neutralize the negative charge of the ring and this dispersal of the charge stabilizes the carbanion.



Ar-S_N2 reaction.



- A group that releases electrons tends to intensify the negative charge, destabilizes the carbanion, and thus slows down reaction.



G ($-\text{NH}_2$, $-\text{OH}$, $-\text{OR}$, $-\text{R}$) releases electrons : destabilizes carbanion, deactivates the $\text{Ar-S}_\text{N}2$ reaction.

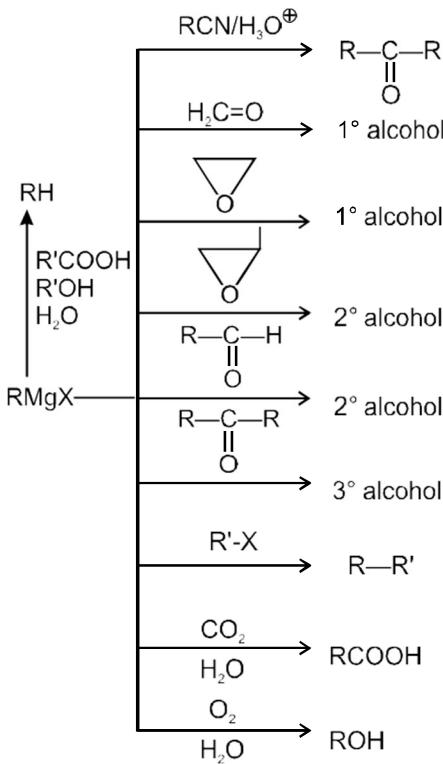
Element effect :

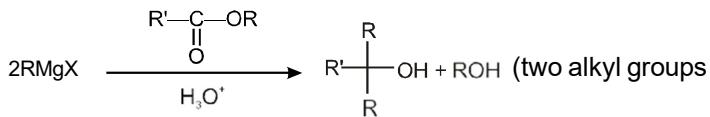
Reactivity order towards $\text{S}_\text{N}2\text{Ar}$ with different halogens
 $\text{Ar-F} > \text{Ar-Cl} > \text{Ar-Br} > \text{Ar-I}$

• Points to remember in Grignard reagents

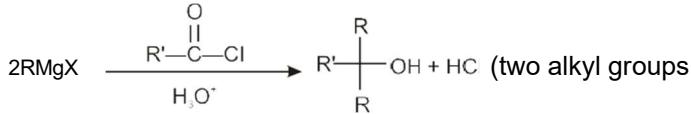
Grignardís Reagent : RMgX (alkyl magnesium halide)

* Active – H Containing compounds $\xrightarrow{\text{RMgX}}$ R-H

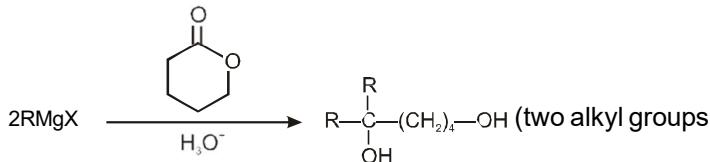




come from Grignard Reagent)



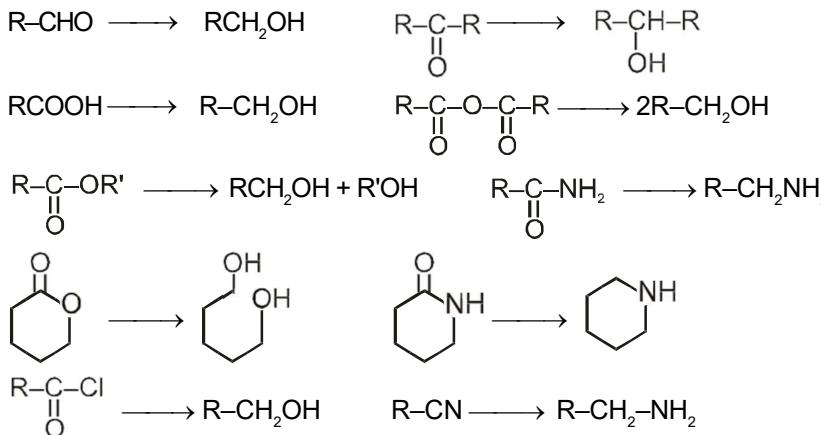
come from Grignard Reagent)



come from Grignard Reagent)

• Points to remember in Reduction

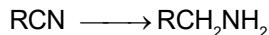
(1) LiAlH_4



(2) $\text{NaBH}_4, \text{EtOH}$



(3) Na/EtOH (Bouveault Blanc reduction)

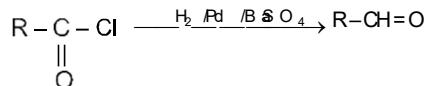


(4) Na/Hg/HCl or

Al[OCHMe₂]₃ (MPV Reduction)

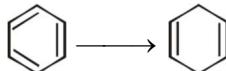
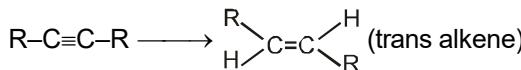


(5) Rossenmundís Reduction



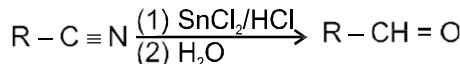
(6) Birch reduction

(Li/Na/K + Liquid NH₃)



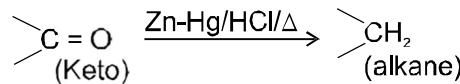
Note : Terminal alkynes not reduced

(7) Stephen's Reduction



Note : DIBAL-H is also used for same conversion.

(8) Clemmensen Reduction



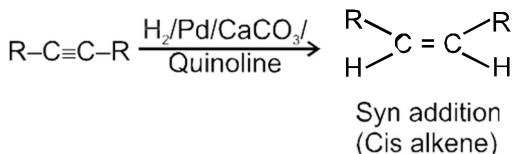
Avoid if acid sensitive groups are present in molecule.
e.g. C=C, C≡C, OH, OR,

(9) Wolff-Kishner Reduction



Avoid if base sensitive groups are present in molecule.
e.g. COOR, COX, CONH,
-CO-O-CO-, R-X

(10) Lindlar Catalyst



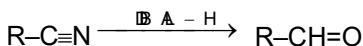
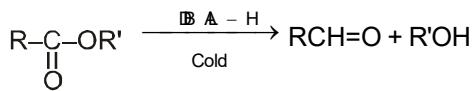
Note : H₂, Pd, BaSO₄ is also used for same conversion.

(11) Red Phosphorus and HI

Almost all functional groups containing compounds convert into corresponding alkane by red P + HI.



(12) DIABAL-H reduction



At ordinary temperature esters reduced to alcohols but at low temperature esters reduced to aldehyde.

• Points to remember in Oxidation Reaction

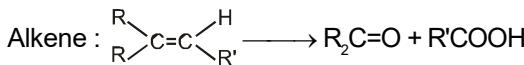
(1) KMnO₄ (in both medium) or K₂Cr₂O₇ (in acidic medium)



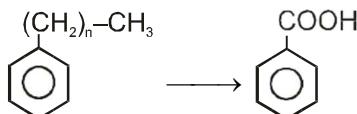
1B Alcohol \longrightarrow Acid

2B Alcohol \longrightarrow Ketone

3B Alcohol \longrightarrow No reaction



Oxidation of aromatic side chain :



(2) PCC (Pyridinium chloro chromate)

CrO₃/HCl/Pyridine

1B ROH \longrightarrow Aldehyde

2B ROH \longrightarrow Ketone

3B ROH \longrightarrow No reaction

(3) Cu/573 K

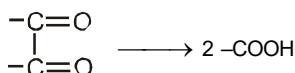
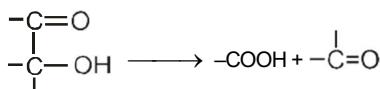
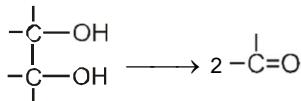
1B Alcohol \longrightarrow Aldehyde

2B Alcohol \longrightarrow Ketone

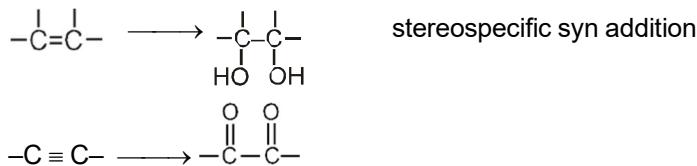
3B Alcohol \longrightarrow Alkene

(4) HIO₄ (Periodic Acid)

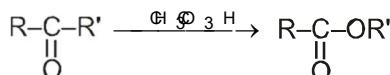
Condition : Vicinal diol, α - Hydroxy ketone & α -diketone can oxidise by HIO₄



(5) Baeyer's reagent and $\text{OsO}_4 + \text{NaHSO}_3$



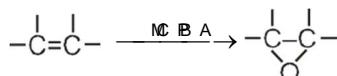
(6) Baeyer-Villiger oxidation (m-CPBA or $\text{CH}_3\text{CO}_3\text{H}$)



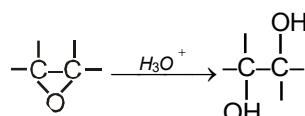
Priority of shift (O accepting aptitude)

$\text{R}' = \text{Ph} > \text{Ethyl} > \text{Methyl}$

(7) Prilezhaev reaction



Anti hydroxylation :



(8) oxidation by HNO_3

Aldehyde \longrightarrow Acid

1B Alcohol \longrightarrow Acid

2B Alcohol \longrightarrow no reaction

3B Alcohol \longrightarrow No reaction

(9) oxidation by MnO_2

1B Alcohol \longrightarrow Aldehyde

2B Alcohol \longrightarrow Ketone

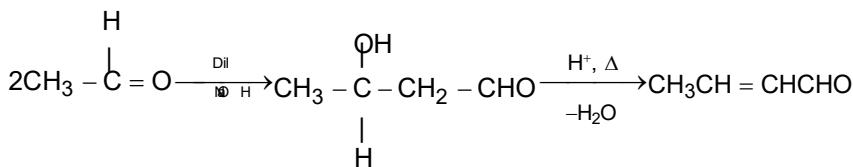
3B Alcohol \longrightarrow No reaction

Note : Only allylic and benzylic alcohols are oxidised by MnO_2 .

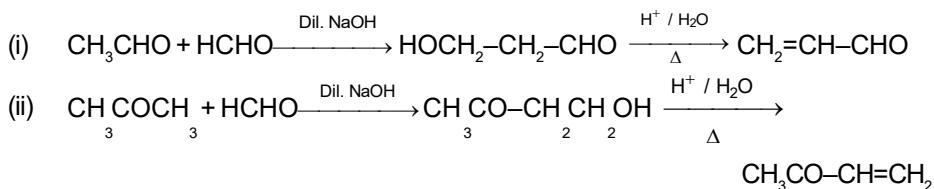
• Points to remember in Aldehyde & ketone

Aldol condensation :

Carbonyl compounds having acidic sp^3 α -H shows this reaction in presence of dil. NaOH or dil. acid.

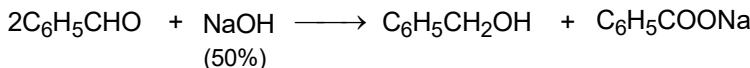
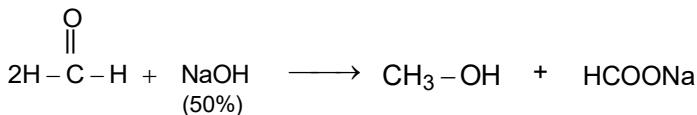


Crossed aldol condensation

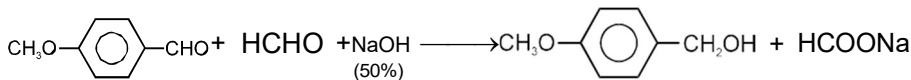


Cannizzaro reaction :

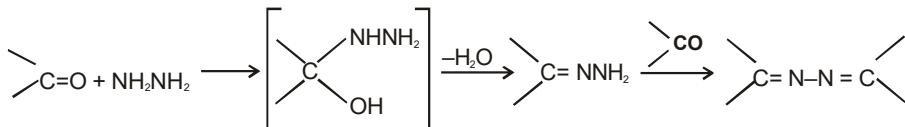
Carbonyl compounds not having $sp^3\alpha$ -H shows following disproportion reaction



Crossed Cannizzaro reaction :



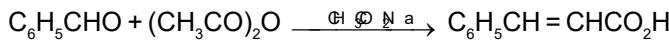
Formation of hydrzones and azines



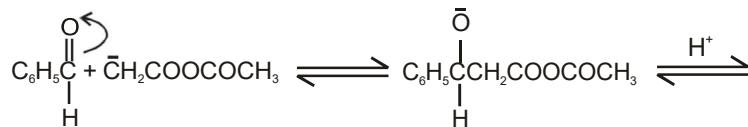
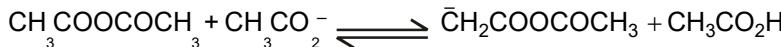
Perkin reaction :

When benzaldehyde (or any other aromatic aldehyde) is heated with the

anhydride of an aliphatic acid (containing two α -hydrogen atoms) in the presence of its sodium salt, condensation takes place to form a β -arylacrylic acid ; e.g., with acetic anhydride and sodium acetate, cinnamic acid is formed.



Mechanism :



Haloform reaction :

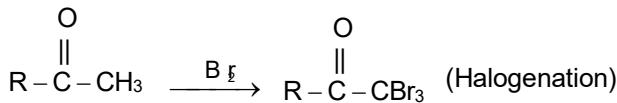
Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl_2 , Br_2 or I_2) in the presence of alkali to give haloform and acid salt.



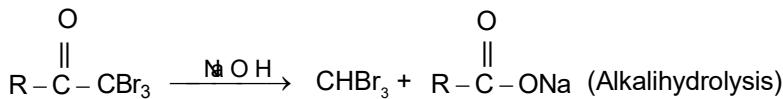
In this reaction $-\text{CH}_3$ of $\text{CH}_3-\text{C}-$ group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone.

Preparation of haloform from methylketone involves two steps.

(a) Halogenation

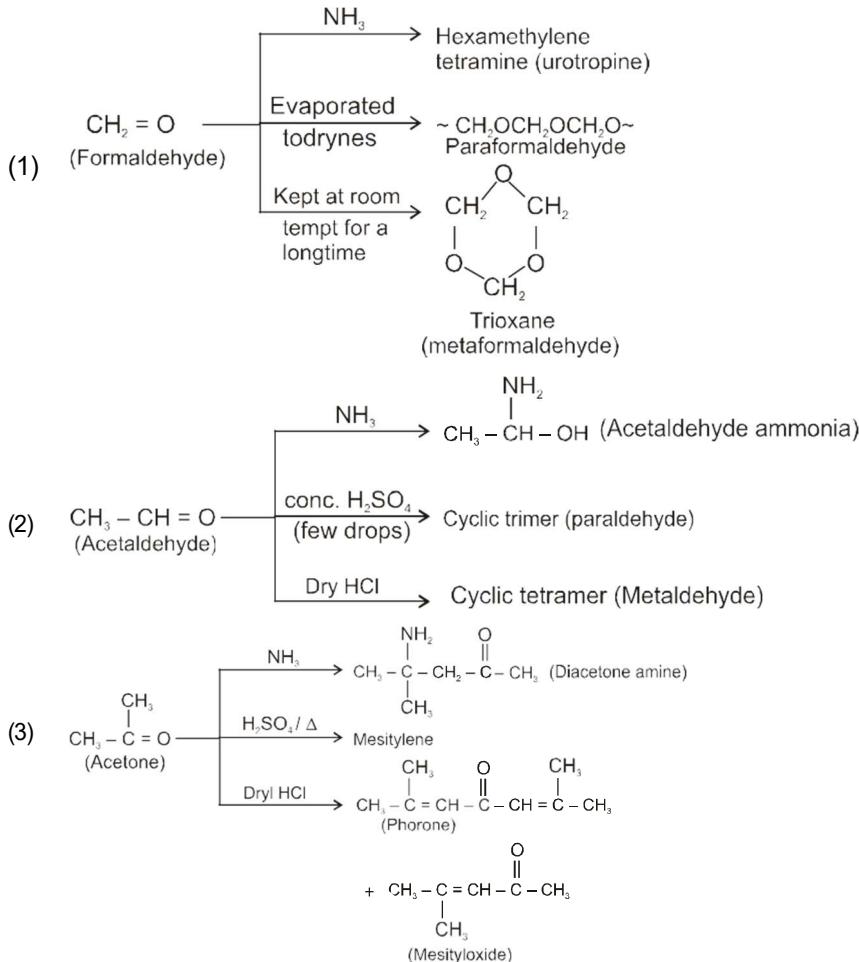


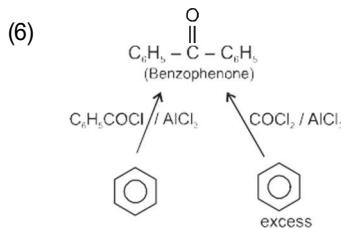
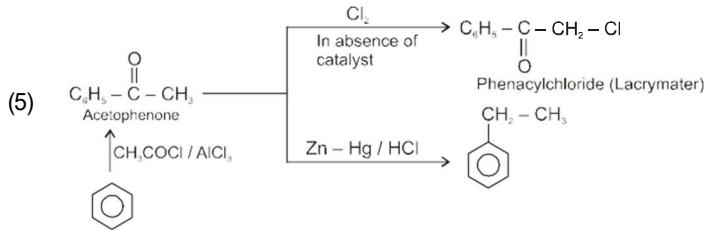
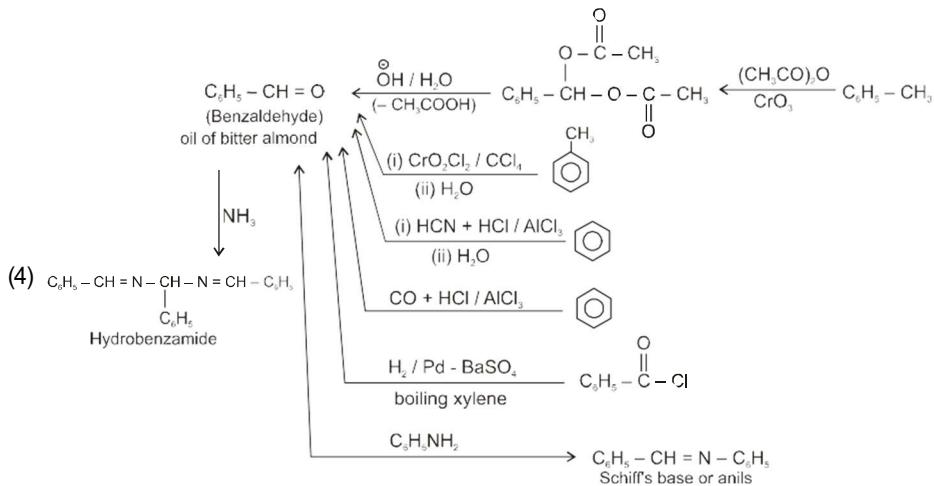
(b) Alkalihydrolysis



Note : This reaction is used to distinguish the presence of $\text{CH}_3-\text{C}-$ group.

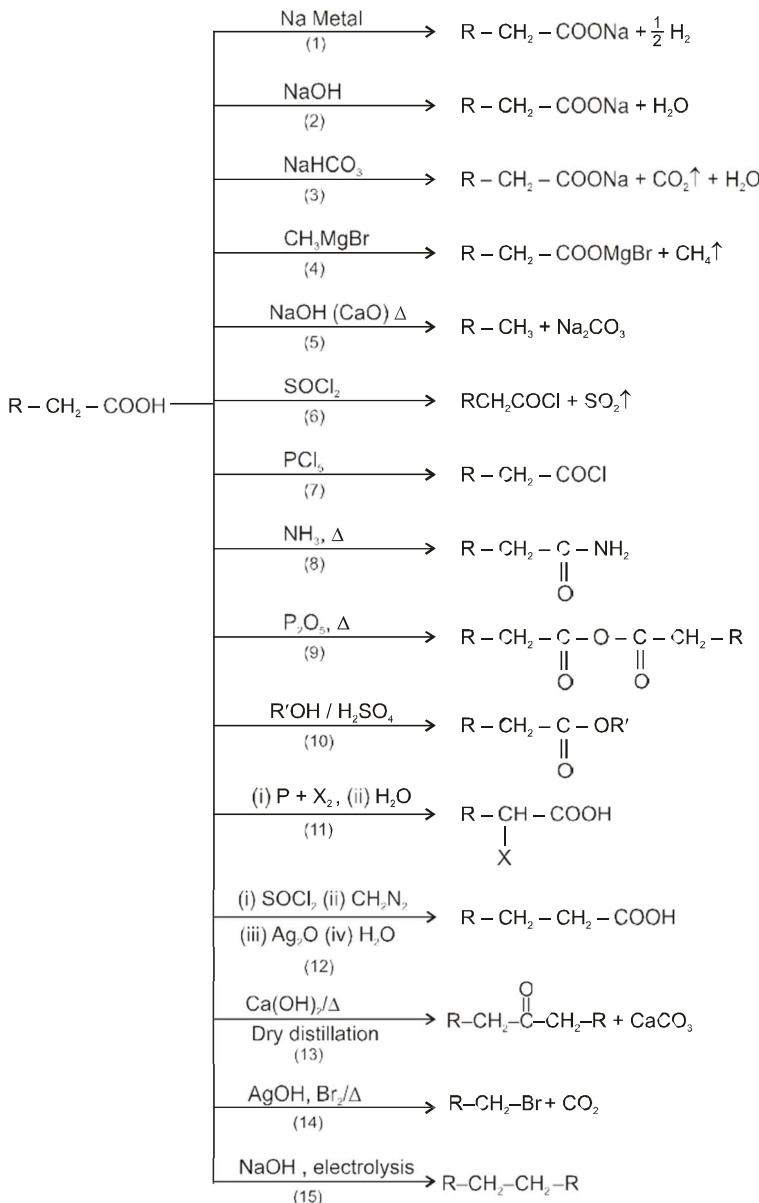
Other reactions :



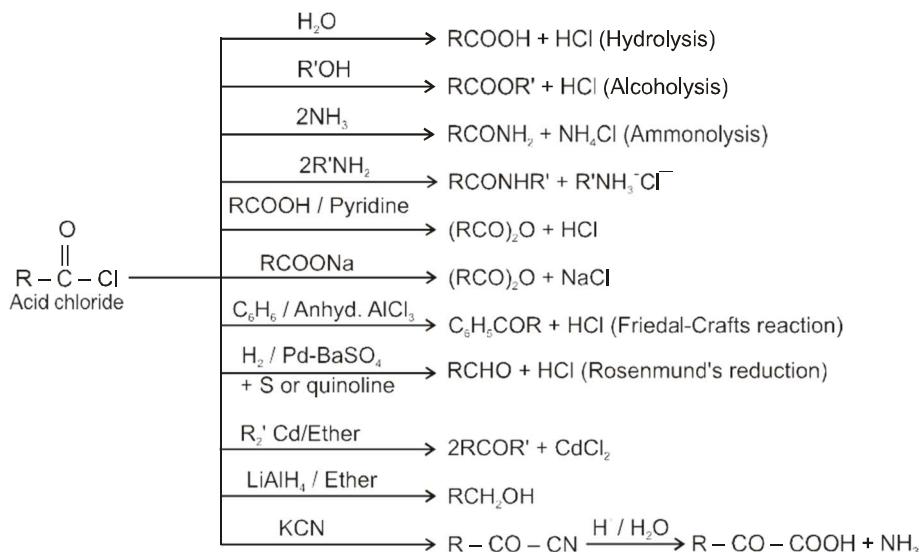


• Points to remember in Carboxylic acid & Derivative

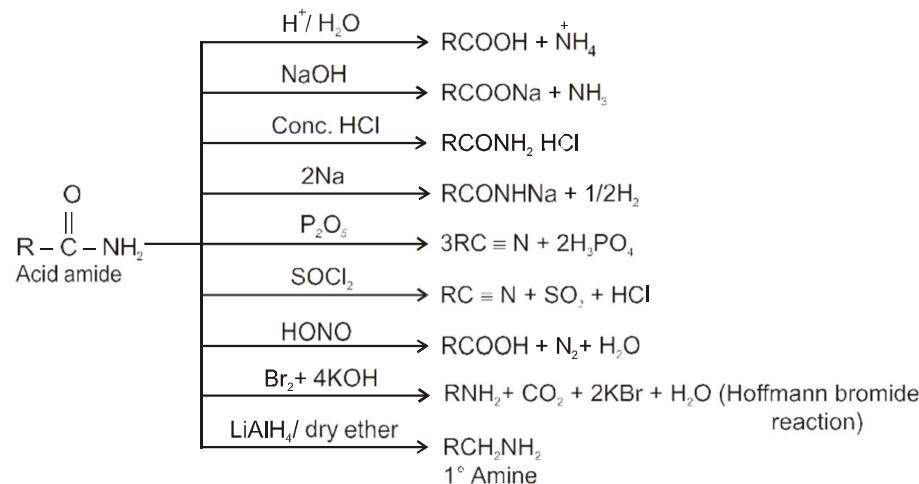
Summary of reactions of carboxylic acids :



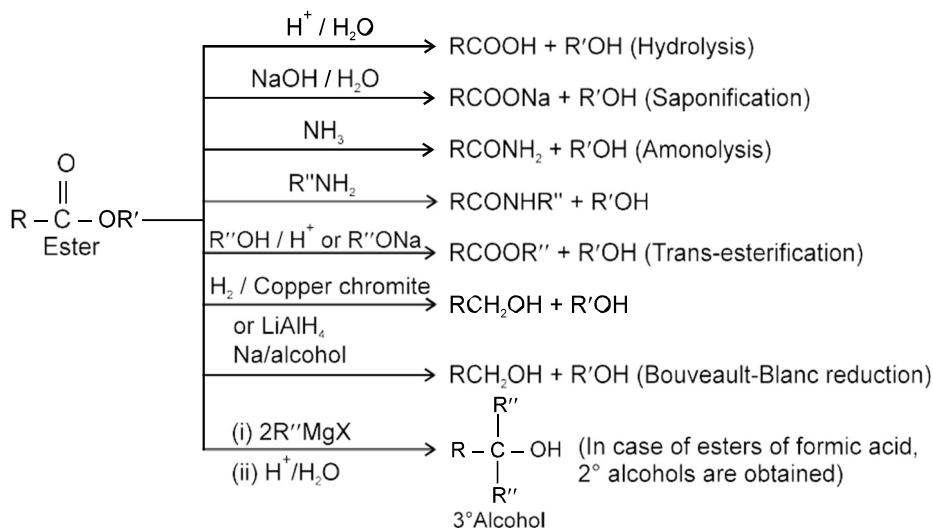
Summary of reactions of acid halide



Summary of reaction of amide:



Summary of reaction of esters :



• Points to remember in Aromatic Compounds

Electrophilic aromatic substitution :

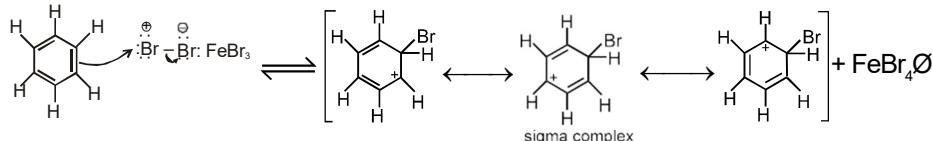
(a) Bromination of Benzene :

Bromination follows the general mechanism for electrophilic aromatic substitution. Bromine itself is not sufficiently electrophilic to react with benzene, but a strong Lewis acid such as FeBr_3 catalyzes the reaction.

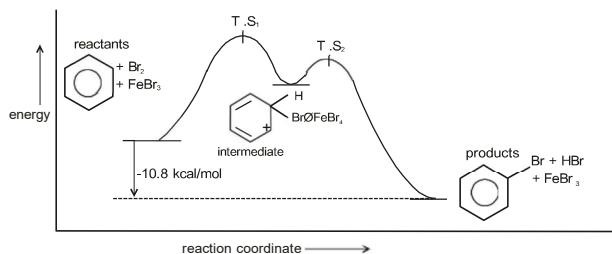
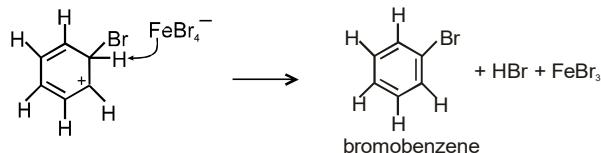
Step 1 : Formation of a stronger electrophile.



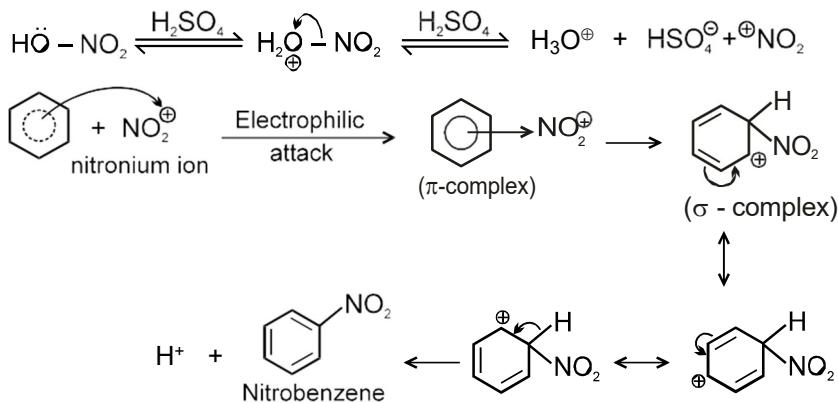
Step 2 : Electrophilic attack and formation of the sigma complex.



Step 3 : Loss of a proton gives the products.

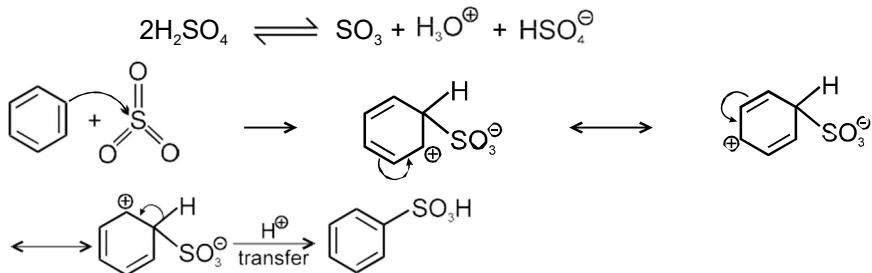


(b) Nitration :



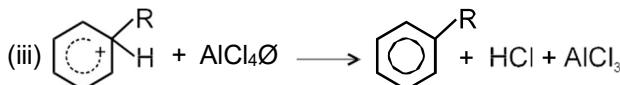
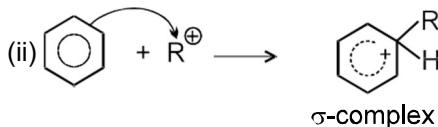
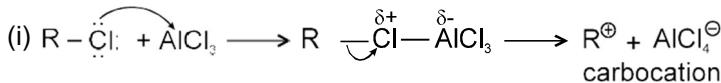
(c) Sulphonation :

The electrophilic reagent, SO_3 , attacks the benzene ring to form the intermediate carbocation.



(d) Friedel Craft reaction :

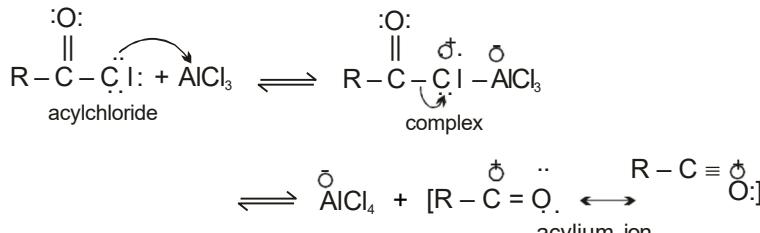
Alkylation mechanism :



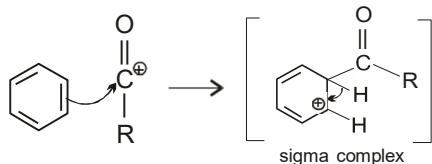
Acylation mechanism :

Acylation of benzene may be brought about with acid chlorides or anhydrides in presence of Lewis acids.

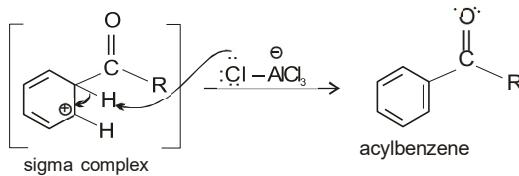
Step 1 : Formation of an acylium ion.

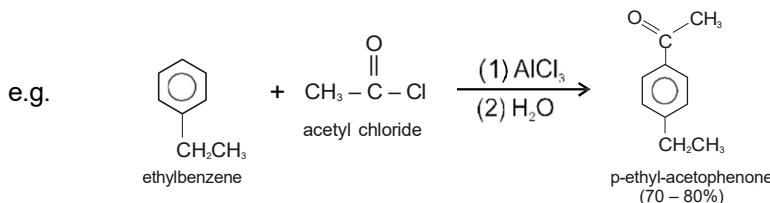


Step 2 : Electrophilic attack.

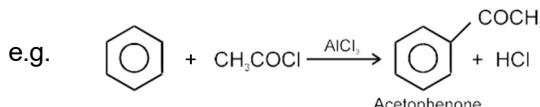


Step 3 : Loss of a proton. Complexation of the product.

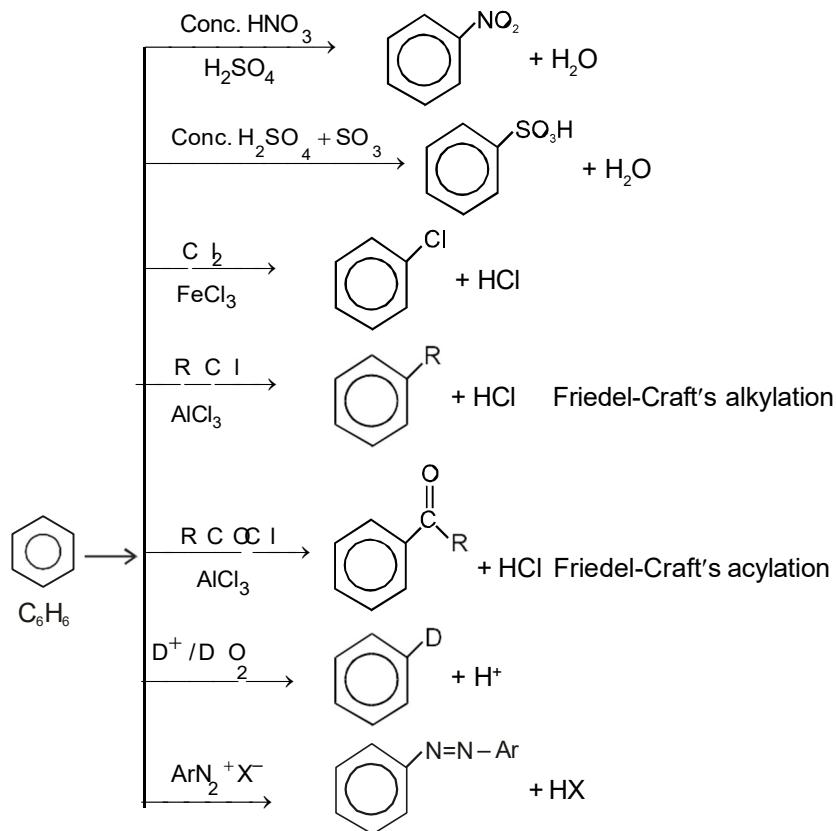




Note : Friedel-Crafts acylations are generally free from rearrangements and multiple substitution. They do not go on strongly deactivated rings.



Chemical Reactions of Benzene :



• Points to remember in Polymers

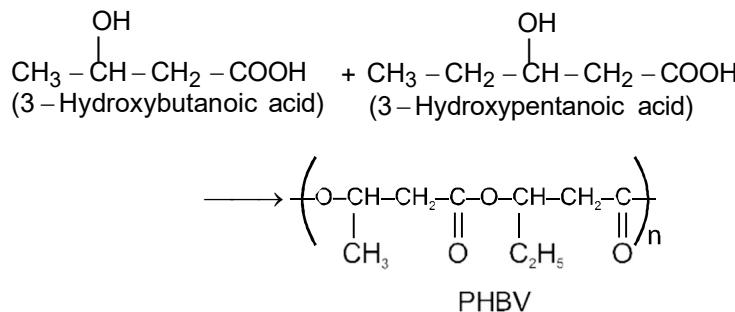
Biodegradable Polymers :

A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric solid waste materials. These solid wastes cause acute environmental problems and remain undegraded for quite a long time. In view of the general awareness and concern for the problems created by the polymeric solid wastes, certain new biodegradable synthetic polymers have been designed and developed. These polymers contain functional groups similar to the functional groups present in biopolymers.

Aliphatic polyesters are one of the important classes of biodegradable polymers. Some examples are given below :

(a) Poly β -hydroxybutyrate – co- β -hydroxy valerate (PHBV) :

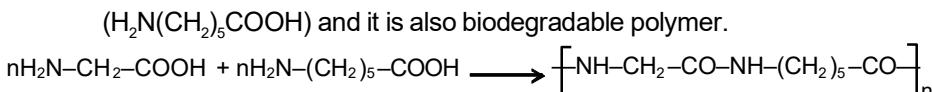
It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.

(b) Nylon-2-nylon-6 :

It is an alternating polyamide copolymer of glycine ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$) and amino caproic acid ($\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$) and it is also biodegradable polymer.



| Some common addition polymers/chain growth polymer | | | | |
|--|---|--|---|--|
| S. No. | Name(s) | Formula | Monomer | Uses |
| 1. | Polyethylene (low density (LDPE)) | $-(CH_2-CH_2)_n-$ | $CH_2=CH_2$ (ethylene) | Film wrap, Plastic Bags |
| 2. | Polyethylene (high density (HDPE)) | $-(CH_2-CH_2)_n-$ | $CH_2=CH_2$ (ethylene) | Electrical insulation bottles, toys |
| 3. | Polypropylene (PP) different grades | $\left[\begin{array}{c} CH_3 \\ \\ CH-CH_2 \end{array} \right]_n$ | $CH_2=CHCH_3$ (propylene) | Manufacture of ropes, toys, pipes, fibres etc. |
| 4. | Poly vinyl chloride (PVC) | $\left[\begin{array}{c} Cl \\ \\ CH-CH_2 \end{array} \right]_n$ | $CH_2=CHCl$ (vinyl chloride) | Manufacture of rain coats, hand bags, vinyl flooring, water Pipes etc. |
| 5. | Poly vinylidene chloride (Saran A) | $\left[\begin{array}{c} Cl \\ \\ C-CH_2 \\ \\ Cl \end{array} \right]_n$ | $CH_2=CCl_2$ (vinylidene chloride) | Seat covers, films & fibers |
| 6. | Polystyrene (Styron) | $\left[\begin{array}{c} CH_2-CH \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$ | $CH_2=CHC_6H_5$ (styrene) | As insulator, wrapping material, manufactures of toys, radio and Television cabinets |
| 7. | Polyacrylonitrile (PAN, Orlon, Acrilan) | $\left[\begin{array}{c} CN \\ \\ CH-CH_2 \end{array} \right]_n$ | $CH_2=CHCN$ (acrylonitrile) | Rugs, Blankets clothing |
| 8. | Polytetrafluoroethylene (PTFE, Teflon) | $-(CF_2-CF_2)_n-$ | $CF_2=CF_2$ (tetrafluoroethylene) | Non-stick surfaces electrical insulation |
| 9. | Poly methyl methacrylate (PMMA, Lucite, Plexiglas, perspex) | $-[CH_2C(CH_3)CO_2CH_3]_n-$ | $CH_2=C(CH_3)CO_2CH_3$ (methylmethacrylate) | Lighting covers, signs skylights |
| 10. | Poly vinyl acetate (PVAc) | $-(CH_2-CHOCOCH_3)_n-$ | $CH_2=CHOCOCH_3$ (vinyl acetate) | Latex paints, Adhesives |
| 11. | Natural Rubber | $-[CH_2-CH=C(CH_3)-CH_2]_n-$ (cis) | $CH_2=CH-C(CH_3)=CH_2$ (isoprene) | Requires vulcanization for practical use |
| 12. | Neoprene | $-[CH_2-CH=CCl-CH_2]_n-$ | $CH_2=CH-CCl=CH_2$ (chloroprene) | Synthetic rubber, oil resistant seal, gaskets, hoses & conveyor belts |
| 13. | SBR styrene butadiene rubber (Buna-S) | $-[CH_2-\underset{Ph}{\overset{ }{CH}}-CH_2-CH=CH-CH_2]-$ | $H_2C=CHC_6H_5$ and $H_2C=CH-CH=CH_2$ | Tyres, floor tiles, foot wear & cable insulation |
| 14. | Nitrile Rubber (Buna-N) | $-[CH_2-\underset{CN}{\overset{ }{CH}}-CH_2-CH=CH-CH_2]-$ | $H_2C=CHCN$ and $H_2C=CH-CH=CH_2$ | Making oil seals, tank lining and hoses |

| Some condensation polymers/step growth polymers | | | | |
|---|---------------------------------|---|---|--|
| S. | Name(s) | Formula | Monomer | Uses |
| 1. | Polyester/Dacron/Terylene/Mylar | | HO2C-C6H4-CO2H (Terephthalic acid) HO-CH2-CH2-OH Ethylene glycol | Fabric, Tyre cord |
| 2. | Glyptal or Alkyds resin | | HO2C-C6H4-CO2H (Phthalic acid) HO-CH2-CH2-OH | Paints and Lacquers |
| 3. | Polyamide (Nylon 6,6) | $\sim [CO(CH_2)_4CO-NH(CH_2)_6NH]_n \sim$ | HO2C-(CH2)4-CO2H H2N-(CH2)6-NH2 | Parachutes & Clothing |
| 4. | Nylon 6,10 | $\sim C-(CH_2)_8-C-NH-(CH_2)_6-NH \sim$ | HOOC-(CH2)8-COOH H2N-(CH2)6-NH2 | |
| 5. | Polyamide Nylon 6, Perlon-L | $\sim [CO(CH_2)_3NH]_n \sim$ | | Rope & Tyre cord |
| 6. | Bakelite | | PhOH + HCHO in (excess) | Electrical Switch, combs, Handle of Utensils, computer discs and Bowling Balls |
| 7. | Urea-formaldehyde resin | $\sim (-NH-CO-NH-CH_2)_n$ | H2N-CO-NH2 (Urea) HCHO (Formaldehyde) | Making unbreakable cups and laminated sheets. |
| 8. | Melamine formaldehyde resin | | +HCHO (formaldehyde) | Unbreakable crockery |
| 9. | Polyamide Kevlar | | Para HO2C-C6H4-CO2H | Tyre |
| 10. | Polyamide Normex | | Meta HO2C-C6H4-CO2H Meta H2N-C6H4-NH2 | |
| 11. | Polyurethane Spandex | | | Foams, Shoes, Automobile seats and components |
| 12. | Polycarbonate Lexan | | (HO-C6H4-C(CH3)2-C(=O)-)2 (Bisphenol A) X2C=O (X = OCH3 or Cl) | Bike helmet, goggles, bullet proof glass |