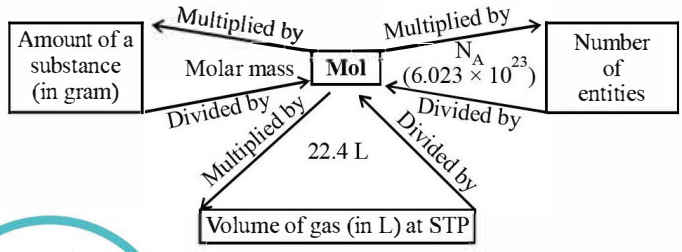


SOME BASIC CONCEPTS OF CHEMISTRY

- Molecular mass

$$= \frac{\text{Average relative mass of one molecule}}{\frac{1}{12} \times \text{mass of C-12 atom}}$$

- Molecular mass = 2 × VD
- Eq. wt. of metal

$$= \frac{\text{wt. of metal}}{\text{wt. of } H_2 \text{ displaced}} \times 1.008$$

- Eq. wt. of metal $= \frac{\text{wt. of metal}}{\text{wt. of oxygen combined}} \times 8$

$$= \frac{\text{wt. of metal}}{\text{wt. of chlorine combined}} \times 35.5$$

- Molecular formula = $(\text{Empirical formula})_n$

ATOMIC STRUCTURE

- Energy of electron in species with one electron.

$$E_n = \frac{-2\pi^2 me^4 Z^2}{n^2 h^2}$$

For energy in SI system,

$$E_n = \frac{-2\pi^2 me^4 Z^2}{n^2 h^2 (4\pi\varepsilon_0)^2}$$

$$E_n = \frac{-1312 Z^2}{n^2} \text{ kJ mol}^{-1}$$

$$mvr = \frac{nh}{2\pi}$$

- $r = \frac{n^2 h^2}{4\pi^2 mZe^2} = 0.529 \left(\frac{n^2}{Z}\right) \text{Å}$
- Total energy of electron in the nth shell

$$= \text{K.E.} + \text{P.E.} = kZ\frac{e^2}{2r_n} + \left(-\frac{kZe^2}{r_n}\right) = -\frac{kZe^2}{2r_n}$$

- $\bar{\upsilon} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$, $[R = 1.0968 \times 10^7 \text{ m}^{-1}]$

$$E = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{h}{\sqrt{2m \times \text{K.E.}}}$$

- No. of spectral lines produced when an electron drops from n^{th} level to ground level $= \frac{n(n-1)}{2}$
- Heisenberg's Uncertainty Principle $(\Delta x)(\Delta p) \geq h/4\pi$
- Nodes $(n - 1)$ = total nodes, ℓ = angular nodes, $(n - \ell - 1)$ = Radial nodes
- Orbital angular momentum : $\sqrt{\ell(\ell+1)}\frac{h}{2\pi} = \sqrt{\ell(\ell+1)}h$

CHEMICAL BONDING

- (i) % ionic character

$$= \frac{\text{Actual dipole moment}}{\text{Calculated dipole moment}} \times 100$$

(ii) Dipole moment is helpful in predicting geometry and polarity of molecule.

- **Fajan's Rule :** Following factors are helpful in increasing covalent character in ionic compounds
  (i) Small cation (ii) Big anion
  (iii) High charge on cation/anion
  (iv) Cation having pseudo inert gas configuration $(ns^2p^6d^{10})$ e.g. Cu^+, Ag^+, Zn^{+2}, Cd^{+2}
- **M.O. theory :**
  (i) Bond order = $\frac{1}{2}(N_b - N_a)$
  (ii) Higher the bond order, higher is the bond dissociation energy, greater is the stability, shorter is the bond length.
- Formal charge (F.C.) on an atom in a Lewis structure
  = [total number of valence electrons in the free atoms]
  – [total number of non-binding (lone pair) electrons]
  – $\frac{1}{2}$[total number of bonding (shared) electrons]
- **Relative bond strength :** $sp^3d^2 > dsp^2 > sp^3 > sp^2 > sp > p\text{-}p$ (Co-axial) > s - p > s - s > p - p (Co-lateral)

VSEPR theory

(i) (LP-LP) repulsion > (LP-BP) > (BP-BP)

(ii) $NH_3 \rightarrow$ Bond Angle 106° 45' because (LP-BP) repulsion > (BP-BP) $H_2O \rightarrow$ 104° 27' because (LP-LP) repulsion > (LP-LB) > (BP-BP)

Hybridisation :

$$= \frac{1}{2}\left(\begin{array}{c}\text{number of valence electrons of central atom} \\ + \text{number of monovalent atoms attached to it} \\ + \text{negative charge if any} - \text{positive charge if any}\end{array}\right)$$

CHEMICAL EQUILIBRIUM

- $K_p = K_c(RT)^{\Delta n_g}$ where $\Delta n_g = n_P - n_R$
- Free Energy Change (ΔG)
  - (a) If $\Delta G = 0$ then reversible reaction would be in equilibrium, $K_c = 0$
  - (b) If $\Delta G = (+)$ ve then equilibrium will be displaced in backward direction; $K_c < 1$
  - (c) If $\Delta G = (-)$ ve then equilibrium will shift in forward direction; $K_c > 1$
- (a) K_c unit $\rightarrow$ (moles/lit)$^{\Delta n}$,
  (b) K_p unit $\rightarrow$ (atm)$^{\Delta n}$
- **Reaction Quotient and Equilibrium Constant**

Consider the following reversible reaction

$$A + B \rightleftharpoons C + D$$

$$\therefore \quad Q_c = \frac{[C][D]}{[A][B]}$$

Case I : If $Q_c < K_c$ then : [Reactants] > [Products] then the system is not at equilibrium

Case II : If $Q_c = K_c$ then : The system is at equilibrium.

Case III : If $Q_c > K_c$ then : [Products] > [Reactants] The system is not at equilibrium.

- A relationship between the equilibrium constant K_C, reaction quotient and Gibb's energy.

$\Delta G = \Delta G° + RT \ln Q$

At equilibrium $\Delta G = 0$ and $Q = K$ then

$\Delta G° = -RT \ln K_c$

$\therefore \quad \Delta G° = -RT \ln K_p$

- Le-Chatelier's principle
  - (i) Increase of reactant conc. (Shift reaction forward)
  - (ii) Decrease of reactant conc. (Shift reaction backward)
  - (iii) Increase of pressure (from more moles to less moles)
  - (iv) Decrease of pressure (from less moles to more moles)
  - (v) For exothermic reaction decrease in temp. (Shift forward)
  - (vi) For endothermic increase in temp. (Shift backward)

IONIC EQUILIBIRIUM

- (i) Lewis Acid (e^- pair acceptor) $\rightarrow$ CO_2, BF_3, $AlCl_3$, $ZnCl_2$, normal cation
  (ii) Lewis Base (e^- pair donor) $\rightarrow$ NH_3, ROH, ROR, H_2O, RNH_2, normal anions
- Dissociation of Weak Acid and Weak Base
  - (i) Weak Acid, $K_a = Cx^2/(1-x)$ or $K_a = Cx^2$; $x << 1$
  - (ii) Weak Base, $K_b = Cx^2/(1-x)$ or $K_b = Cx^2$; $x << 1$
- Buffer solution {Henderson equation} :
  - (i) Acidic, $pH = pK_a + \log$ {Salt/Acid}.
    For maximum buffer action $pH = pK_a$
    Range of buffer $pH = pK_a \pm 1$
  - (ii) Alkaline $\rightarrow pOH = pK_b + \log$ {Salt/Base} for max. buffer action $pH = 14 - pK_b$
    Range $pH = 14 - pK_b \pm 1$
  - (iii) Buffer Capacity $= \dfrac{\text{Moles / lit of Acid or Base Mixed}}{\text{Change in pH}}$
- Relation between ionisation constant (K_i) and degree of ionisation(α):-

$$K_i = \frac{\alpha^2}{(1-\alpha)V} = \frac{\alpha^2 C}{(1-\alpha)} \text{ (Ostwald's dilution law)}$$

It is applicable to weak electrolytes for which $\alpha << 1$ then

$$\alpha = \sqrt{K_i V} = \sqrt{\frac{K_i}{C}} \text{ or } V\uparrow C\downarrow \alpha\uparrow$$

- **Common ion effect :** By addition of X mole/L of a common ion, to a weak acid (or weak base) α becomes equal to $\frac{K_a}{X}\left(\text{or } \frac{K_b}{X}\right)$ [where α = degree of dissociation]
- (i) If solubility product > ionic product then the solution is unsaturated and more of the substance can be dissolved in it.
  (ii) If ionic product > solubility product the solution is super saturated (principle of precipitation).
- Salt of weak acid and strong base :

$$pH = 0.5\,(pK_w + pK_a + \log c);\ h = \sqrt{\frac{K_h}{c}}\ ;\ K_h = \frac{K_w}{K_a}$$

(h = degree of hydrolysis)

Salt of weak base and strong acid :

$$pH = 0.5\,(pK_w - pK_b - \log c);\ h = \sqrt{\frac{K_w}{K_b \times c}}$$

Salt of weak acid and weak base :

$$pH = 0.5\,(pK_w + pK_a - pK_b);\ h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

CHEMICAL KINETICS

- **Unit of rate constant :**
  $k = \text{mol}^{1-n}\ \text{lit}^{n-1}\ \text{sec}^{-1}$
- **Order of reaction** It can be fraction, zero or any whole number.
- **Molecularity of reaction** is always a whole number. It is never more than three. It cannot be zero.
- **First Order Reactions :**

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)} \ \&\ t_{1/12} = \frac{0.693}{k}$$

$$[A]_t = [A]_0 e^{-kt}$$

- **Second Order Reactions :**

When concentration of A and B taking same.

$$k_2 = \frac{1}{t}\left(\frac{x}{a(a-x)}\right)$$

When concentration of A and B are taking different -

$$k_2 = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$$

- **Zero Order Reaction :** $x = kt$ and $t_{1/2} = \frac{a}{2k}$
  The rate of reaction is independent of the concentration of the reacting substance.
- Time of nth fraction of first order process,

$$t_{1/n} = \frac{2.303}{k} \log\left(\frac{1}{1-\frac{1}{n}}\right)$$

- Amount of substance left after 'n' half lives $= \frac{[A]_o}{2^n}$
- **Arrhenius equation :** $k = Ae^{-E_a/RT}$, slope $= \frac{-E_a}{2.303R}$
  and Temperature Coefficient

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

- It has been found that for a chemical reaction with rise in temperature by 10 °C, the rate constant gets nearly doubled.

$$k = PZ_{AB}e^{-E_a/RT}$$

OXIDATION - REDUCTION

- Oxidant itself is reduced (gives O_2)
  Or Oxidant $\longrightarrow e^-$ (s) Acceptor
  Reductant itself is oxidised (gives H_2)
  Or reductant $\longrightarrow e^-$ (s) Donor
- (i) Strength of acid $\propto$ O.N
  (ii) Strength of base $\propto$ 1/ O.N
- (i) Electrochemical Series:- Li, K, Ba, Sr, Ca, Na, Mg, Al, Mn, Zn, Cr, Fe, Cd, Co, Ni, Sn, Pb, H_2, Cu, Ag, Pt, Au.

(ii) As we move from top to bottom in this series
(a) Standard Reduction Potential ↑
(b) Standard Oxidation Potential ↓
(c) Reducing Capacity ↓
(d) IP ↑
(e) Reactivity ↓

THERMO-DYNAMICS

- First Law of Thermodynamics :
  $\Delta E = Q + W$
  Expression for pressure volume work
  $W = -P\Delta V$
  Maximum work in a reversible expansion :

$$W = -2.303n\,RT \log \frac{V_2}{V_1}$$

$$= -2.303\,nRT \log \frac{P_1}{P_2}$$

$$W_{rev} \geq W_{irr}$$

- $q_v = c_v\Delta T = \Delta U$, $q_p = c_p\Delta T = \Delta H$

Enthapy changes during phase transformation
(i) Enthalpy of Fusion
(ii) Heat of Vapourisation
(iii) Heat of Sublimation

- **Enthalpy :** $\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n_g RT$
- **Kirchoff's equation :**

$$\Delta E_{T_2} = \Delta E_{T_1} + \Delta C_V\ (T_2 - T_1)\ [\text{constant V}]$$

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_P\ (T_2 - T_1)\ [\text{constant P}]$$

- **Entropy(s) :** Measure of disorder or randomness
  $\Delta S = \Sigma S_p - \Sigma S_R$

$$\Delta S = \frac{q_{rev}}{T} = 2.303\,nR \log \frac{V_2}{V_1} = 2.303\,n\,R \log \frac{P_1}{P_2}$$

- Free energy change : $\Delta G = \Delta H - T\Delta S$, $\Delta G^o = -nFE^o_{cell}$
  $-\Delta G = W(\text{maximum}) - P\Delta V$, $\Delta G_{system} = -T\Delta S_{total}$

ΔH	ΔS	ΔG	Reaction characteristics
–	+	Always negative	Reaction is spontaneous at all temperature.
+	–	Always positive	Reaction is nonspontaneous at all temperature
–	–	Negative at low temperature but positive at high temperature	Spontaneous at low temp. & non spontaneous at high temperature
+	+	Positive at low temp. but negative at high temperature	Non spontaneous at low temp. & spontaneous at high temp.

ELECTRO-CHEMISTRY

- $m = Z.I.t$
- Degree of dissociation : $\alpha = \frac{\lambda_{eq}}{\lambda^0_{eq}}$
- Specific conductance

$$\kappa = \frac{1}{\rho} = \frac{\ell}{R.a} = G \times \frac{\ell}{a} = G \times \text{cell constant (G*)};$$

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

- Kohlrausch's law : $\Lambda^0_m = x\lambda^0_A + y\lambda^0_B$
- Nernst Equation

$$E = E^o - \frac{0.0591}{n}\log_{10}\frac{[\text{Products}]}{[\text{Reactants}]}$$

$$\&\ E^o_{Cell} = E^o_{right} + E^o_{left}\ \&\ K_{eq.} = \text{antilog}\left[\frac{nE^o}{0.0591}\right]$$

$$\Delta G = -nFE_{cell}\ \&\ \Delta G^o = -nFE^o\,\text{cell} = -2.303\,RT\log K_c$$

$$\&\ W_{max} = +nFE^o\ \&\ \Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

- Calculation of pH of an electrolyte by using a calomel electrode : $pH = \frac{E_{cell} - 0.2415}{0.0591}$
- Thermodynamic efficiency of fuel cells :

$$\eta = \frac{-\Delta G}{\Delta H} = \frac{-nFE^o_{cell}}{\Delta H}$$

For H_2–O_2 fuel cells it is 95%.

- $P = K_H . x$
- Normality (N) $= \frac{\text{number of equivalents}}{\text{volume of the solution in litres}}$
- Molarity (M) $= \frac{\text{number of moles}}{\text{volume of the solution in litres}}$

SOLUTION AND COLLIGATIVE PROPERTIES

- Raoult's law
  $P = p_A + p_B = p°_A X_A + p°_B X_B$
- **Characteristics of an ideal solution:**
  (i) $\Delta_{sol}V = 0$ (ii) $\Delta_{sol}H = 0$
- Relative lowering of vapour pressure
  $= \frac{P_A^o - P_A}{P_A^o}$
  $\frac{P_A^o - P_A}{P_A^o} = X_B = \frac{n_B}{n_A + n_B}$
- Colligative $\propto$ Number of particles/ ions/ moles of solute properties
- Depression of freezing point, $\Delta T_f = K_f m$
- Elevation in boiling point with relative lowering of vapour pressure
  $\Delta T_b = \frac{1000K_b}{M_1}\left(\frac{p^o - p}{p^o}\right)$ (M_1 = mol. wt. of solvent)
- Osmotic pressure (P) with depression in freezing point ΔT_f
  $P = \Delta T_f \times \frac{dRT}{1000K_f}$
- Relation between Osmotic pressure and other colligative properties:
  (i) $\pi = \left(\frac{p_A^o - p_A}{p_A^o}\right) \times \frac{dRT}{M_B}$ Relative lowering of vapour pressure
  (ii) $\pi = \Delta T_b \times \frac{dRT}{1000K_b}$ Elevation in boiling point
  (iii) $\pi = \Delta T_f \times \frac{dRT}{1000K_f}$ Depression in freezing point
- $i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$
- Degree of association $a = (1 - i)\frac{n}{n-1}$
  & degree of dissociation $(\alpha) = \frac{i-1}{n-1}$

GASEOUS STATE

- Ideal gas equation : $PV = nRT$
  (i) $R = 0.0821$ liter atm. deg^{-1} $mole^{-1}$
  (ii) $R = 2$ cals. $deg.^{-1}$ $mole^{-}$
  (iii) $R = 8.314\ JK^{-1}$ $mole^{-1}$
- Velocities related to gaseous state
  RMS velocity $= \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$
  Average speed $= \sqrt{\frac{8RT}{M}}$ & Most probable speed $= \sqrt{\frac{2RT}{M}}$
  Average speed = 0.9213 × RMS speed
  RMS speed = 1.085 × Average speed
  MPS = .816 × RMS; RMS = 1.224 MPS
  MPS : A.V. speed : RMS = 1 : 1.128 : 1.224
- Rate of diffusion $\propto \frac{1}{\sqrt{\text{density of gas}}}$
- van der Waal's equation
  $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$ for n moles
- Z (compressibility factor) $= \frac{PV}{nRT}$; Z = 1 for ideal gas
  $T_C = \frac{8a}{27Rb}$, $P_C = \frac{a}{27b^2}$, $V_C = 3b$, $T_b = \frac{a}{bR}$

SOLID AND LIQUID STATE

- Available space filled up by hard spheres (packing fraction):
  Simple cubic $= \frac{\pi}{6} = 0.52$
  $bcc = \frac{\pi\sqrt{3}}{8} = 0.68$ $fcc = \frac{\pi\sqrt{2}}{6} = 0.74$
  $hcp = \frac{\pi\sqrt{2}}{6} = 0.74$
  diamond $= \frac{\pi\sqrt{3}}{6} = 0.34$
- Radius ratio and co-ordination number (CN)

Limiting radius ratio	CN	Geometry
[0.155–0.225]	3	[Plane triangle]
[0.255–0.414]	4	[Tetrahedral]
[0.414–0.732]	6	[Octahedral]
[0.732–1]	8	[*bcc*]

- Atomic radius *r* and the edge of the unit cell:
  Pure elements :
  Simple cubic $= r = \frac{a}{2}$; $bcc\ r = \frac{\sqrt{3}a}{4}$; $fcc = \frac{\sqrt{2}a}{4}$
- Relationship between radius of void (*r*) and the radius of the sphere (*R*) : *r* (tetrahedral) = 0.225 *R* ; *r* (octahedral) = 0.414 *R*
- Paramagnetic : Presence of unpaired electrons [attracted by magnetic field]
- Ferromagnetic : Permanent magnetism [↑↑↑↑]
- Antiferromagnetic : Net magnetic moment is zero [↑↓↑↓]
- **Ferrimagnetic :** Net magnetic moment is three [↑↓↓↑↑]

SURFACE CHEMISTRY & COLLOIDAL STATE

- **Emulsion :** Colloidal soln. of two immiscible liquids [O/W emulsion, W/O emulsion]
- **Emulsifier :** Long chain hydrocarbons are added to stabilize emulsion.
- **Lyophilic colloid :** Starchy gum, gelatin have greater affinity for solvent.
- **Lyophobic colloid :** No affinity for solvent, special methods are used to prepare sol. [e.g. As_2S_3, $Fe(OH)_3$ sol]
- **Preparation of colloidal solution :**
  (i) Dispersion methods (ii) Condensation method.
- **Coagulating power** $\propto \frac{1}{\text{Flecculating value}}$
- **Properties of colloidal solution :**
  (i) Tyndall effect (ii) Brownian movement
  (iii) Coagulation (iv) Filtrability.

INORGANIC CHEMISTRY

PERIODIC TABLE

- General electronic configuration (of outer orbits)
  - s-block ns^{1-2}
  - p-block ns^2np^{1-6}
  - d-block $(n-1)d^{1-10}\ ns^{1-2}$
  - f-block $(n-2)f^{1-14}s^2p^6d^{10}$
    $(n-1)s^2p^6d^{0\ \text{or}\ 1}\ ns^2$
-

Property	Pr (L To R)	Gr (T to B)
(i) Atomic radius	↓	↑
(ii) Ionisation potential	↑	↓
(iii) Electron affinity	↑	↓
(iv) Electronegativity	↑	↓
(v) Metallic character or electropositive character	↓	↑
(vi) Alkaline character of hydroxides	↓	
(vii) Acidic character	↑	↓
(viii) Reducing property	↓	↑
(ix) Oxidising property	↑	↓
(x) Non metallic character	↑	↓

- $IP \propto \dfrac{1}{\text{Metallic character}} \propto \dfrac{1}{\text{Reducing character}}$
- $EA \propto \dfrac{1}{\text{size}} \propto$ nuclear charge.
  Second electron affinity is always negative.
  Electron affinity of chlorine is greater than fluorine (small atomic size).
- The first element of a group has similar properties with the second element of the next group. This is called diagonal relationship. The diagonal relationship disappears after IV group.

s-BLOCK ELEMENTS

- Atomic radii : Li < Na < K < Rb < Cs
- Electronegativity : Li > Na > K > Rb > Cs
- First ionization potential : Li > Na > K > Rb > Cs
- Melting point Li > Na > K > Rb > Cs
- Colour of the flame Li - Red, Na - Golden, K - Violet, Rb - Red, Cs - Blue, Ca - Brick red, Sr - Blood red, Ba-Apple green
- Rb and Cs show photoelectric effect.
- Stability of hydrides : LiH > NaH > KH > RbH > CsH
- Basic nature of hydroxides : LiOH < NaOH < KOH < RbOH < CsOH
- **Hydration energy :** Li > Na > K > Rb > Cs
- **Reducing character :** Li > Cs > Rb > K > Na

BORON FAMILY

- Stability of +3 oxidation state :
  B > Al > Ga > In > Tl
- Stability of +1 oxidation state :
  Ga < In < Tl
- Basic nature of the oxides and hydroxides :
  B < Al < Ga < In < Tl
- Relative strength of Lewis acid :
  $BF_3 < BCl_3 < BBr_3 < BI_3$
- **Ionisation energy : B > Al < Ga > In < Tl**
- **Electronegativity :** Electronegativity first decreases from B to Al and then increases marginally.

CARBON FAMILY

- Reactivity : C < Si < Ge < Sn < Pb
- Metallic character : C < Si < Ge < Sn < Pb
- Acidic character of the oxides :
  $CO_2 > SiO_2 > GeO_2 > SnO_2 > PbO_2$
  Weaker acidic (amphoteric)
- Reducing nature of hydrides
  $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$
- Thermal stability of tetrahalides
  $CCl_4 > SiCl_4 > GeCl_4 > SnCl_4 > PbCl_4$
- Oxidising character of M^{+4} species
  $GeCl_4 < SnCl_4 < PbCl_4$
- Ease of hydrolysis of tetrahalides
  $SiCl_4 < GeCl_4 < SnCl_4 < PbCl_4$

NITROGEN FAMILY

- Acidic strength of trioxides : $N_2O_3 > P_2O_3 > As_2O_3$
- Acidic strength of pentoxides
  $N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$
- Acidic strength of oxides of nitrogen
  $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$
- Basic nature, bond angle, thermal stability and dipole moment of hydrides
  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
- Stability of trihalides of nitrogen : $NF_3 > NCl_3 > NBr_3$
- Lewis base strength : $NF_3 < NCl_3 > NBr_3 < NI_3$
- Ease of hydrolysis of trichlorides
  $NCl_3 > PCl_3 > AsCl_3 > SbCl_3 > BiCl_3$
- Lewis acid strength of trihalides of P, As and Sb
  $PCl_3 > AsCl_3 > SbCl_3$
- Lewis acid strength among phosphorus trihalides
  $PF_3 > PCl_3 > PBr_3 > PI_3$
- Nitrogen displays a great tendency to form $p\pi - p\pi$ multiple bonds with itself as well as with carbon and oxygen.
- The basic strength of the hydrides
  $NH_3 > PH_3 > AsH_3 > SbH_3$
- The thermal stability of the hydrides decreases as the atomic size increases.

OXYGEN FAMILY

- Melting and boiling point of hydrides
  $H_2O > H_2Te > H_2Se > H_2S$
- Volatility of hydrides
  $H_2O < H_2Te < H_2Se < H_2S$
- Reducing nature of hydrides
  $H_2S < H_2Se < H_2Te$
- Covalent character of hydrides
  $H_2O < H_2S < H_2Se < H_2Te$
- The acidic character of oxides (elements in the same oxidation state)
  $SO_2 > SeO_2 > TeO_2 > PoO_2$; $SO_3 > SeO_3 > TeO_3$
- Acidic character of oxide of a particular element (e.g. S)
  $SO < SO_2 < SO_3$; $SO_2 > TeO_2 > SeO_2 > PoO_2$

HALOGEN FAMILY

- Bond energy of halogens : $Cl_2 > Br_2 > F_2 > I_2$
- Solubility of halogen in water : $F_2 > Cl_2 > Br_2 > I_2$
- Oxidising power : $F_2 > Cl_2 > Br_2 > I_2$
- Enthalpy of hydration of X^- ion : $F^- > Cl^- > Br^- > I^-$
- Reactivity of halogens : F > Cl > Br > I
- Ionic character of M - X bond in halides
  $M-F > M-Cl > M-Br > M-I$
- Reducing character of X^- ion : $I^- > Br^- > Cl^- > F^-$
- Acidic strength of halogen acids : HI > HBr > HCl > HF
- Conjugate base strength of halogen acids
  $I^- < Br^- < Cl^- < F^-$
- Reducing property of hydrogen halides
  HF < HCl < HBr < HI
- Oxidising power of oxides of chlorine
  $Cl_2O > ClO_2 > Cl_2O_6 > Cl_2O_7$
- Acidic character of oxyacids of chlorine
  $HClO < HClO_2 < HClO_3 < HClO_4$
- Oxidising power of oxyacids of chlorine
  $HClO > HClO_2 > HClO_3 > HClO_4$

NOBLE GASES

- $XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]$
  $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]$
  $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$
  $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$
  $2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + 4HF + F_2$

$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$

$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$

$2XeO_2F_4 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$

TRANSITION ELEMENTS (d- and f-BLOCK ELEMENTS

- The element with exceptional configuration are
  $Cr^{24}[Ar]\,3d^5 4s^1$, $Cu^{29}[Ar]\,3d^{10}4s^1$
  $Mo^{42}[Kr]\,4d^5 5s^1$, $Pd^{46}[Kr]\,4d^{10}5s^0$
  $Ag^{47}[Kr]\,4d^{10}5s^1$, $Pt^{78}[Xe]\,4f^{14}5d^{10}6s^0$
- **Inner Transition Elements**

(i) **Electronic Configuration -**
$[Xe]4f^{0-14}5d^{0-1}6s^2$

(ii) **Magnetic properties -** Magnetic moment is given by the formula $\mu = \sqrt{4S(S+1)+L(L+1)}$

where L = Orbital quantum number, S = Spin quantum number

COORDINATION COMPOUNDS

- Coordination number is the number of the nearest atoms or groups in the coordination sphere.
- Ligand is a Lewis base donor of electrons that bonds to a central metal atom in a coordination compound.
- Paramagnetic substance is one that is attracted to the magnetic field, this results on account of unpaired electrons present in the atom/molecule/ion.
- Effective atomic number EAN
  = (Z – Oxidation number) + (2 × Coordination number)
- Factors affecting stability of complex
  (i) Greater the charge on the central metal ion, greater is the stability.
  (ii) Greater the ability of the ligand to donate electron pair (basic strength) greater is the stability.
  (iii) Formation of chelate rings increases the stability.
- Isomerism in coordination compounds :
  (i) Structural Isomerism (ii) Ionization Isomerism
  (iii) Hydration Isomerism (iv) Linkage Isomerism
  (vii) Polymerisation Isomerism (viii) Valence Isomerism
  (ix) Coordination Position Isomerism
  (x) Stereo Isomerism
  (a) Geometrical
  (1) *Square planar complexes of the type* MA_2X_2 ; $MABX_2$; MABXY
  (2) Octahedral of the type : MA_4XY, MA_4X_2 MA_3X_3 $MA_2X_2Y_2$. $M(AA)_2X_2$ and M(ABCDEF).
  (b) Optical isomerism

ORGANIC CHEMISTRY

GENERAL ORGANIC CHEMISTRY

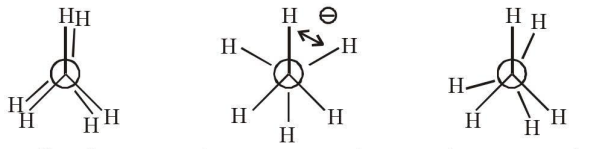
- The order of decreasing electronegativity of hybrid orbitals is $sp > sp^2 > sp^3$.
- Conformational isomers are those isomers which arise due to rotation around a single bond.
- A meso compound is optically inactive, even though it has asymmetric centres (due to internal compensation of rotation of plane polarised light)
- An equimolar mixture of enantiomers is called racemic mixture, which is optically inactive.
- Reaction intermediates and reagents :
  Homolytic fission → Free radicals
  Heterolytic fission → Ions (Carbonium ions, carbanions etc.)
- Nucleophiles – Electron rich
  Two types : (i) Anions (ii) Neutral molecules with lone pair of electrons (Lewis bases)

Electrophiles : Electron deficient.
Two types : (i) Cations (ii) Neutral molecules with vacant orbitals (Lewis acids).

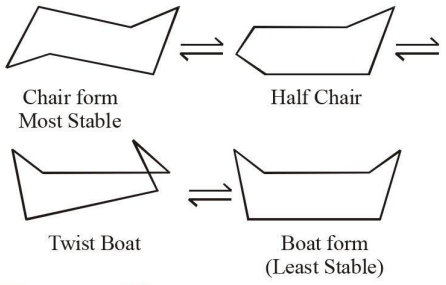
- Inductive effect is due to σ electron displacement along a chain and is permanent effect.
- +I (inductive effect) increases basicity, – I effect increases acidity of compounds.
- Resonance is a phenomenon in which two or more structures can be written for the same compound but none of them actually exists.

ALKANES

- Pyrolytic cracking is a process in which alkane decomposes to a mixture of smaller hydrocarbons, when it is heated strongly, in the absence of oxygen.
- Ethane can exist in an infinite number of conformations. They are



- **Conformations of Cyclohexane :** It exists in two nonplanar, strainless forms, the boat and the chair form



ALKENES

- In dehydration and dehydrohalogenation the preferential order for removal of hydrogen is 3° > 2° > 1° (Saytzeff's rule).
- The lower the ΔH_h (heat of hydrogenation) the more stable the alkene is.
- Alkenes undergo anti-Markonikov addition only with HBr in the presence of peroxides.

ALKYNES

- Alkynes add water molecule in presence of mercuric sulphate and dil. H_2SO_4 and form carbonyl compounds.
- Terminal alkynes have acidic H-atoms, so they form metal alkynides with Na, ammonical cuprous chloride solution and ammoniacal silver nitrate solution.
- Alkynes are acidic because of H-atoms which are attached to sp 'C' atom which has more electronegativity and 's' character than sp^2 and sp^3 'C' atoms.

ARENES

- All o and p-directing groups are ring activating groups (except – X)

  They are : $-OH, -NH_2, -X, -R, -OR$, etc.
- All m-directing groups are ring deactivating groups.

  They are : $-CHO, -COOH, -NO_2, -CN, -\overset{+}{N}R_3$, etc.

HALOGEN COMPOUNDS

- The order of reactivity is

  (i) RI > RBr > RCl > RF

  (i) Allyl halide > Alkyl halide > Vinyl halide

  (iii) Alkyl halide > Aryl halide
- **S_N1 reaction :** Mainly 3° alkyl halides undergo this reaction and form racemic mixture. S_N1 is favoured by polar solvent and low concentration of nucleophile.
- **S_N2 reaction :** Mainly 1° alkyl halides undergo this substitution. Walden inversion takes place. S_N2 reaction is preferred by non-polar solvents and high concentration of nucleophile.
- **Reaction with metals:**

  (*i*) $\underset{\text{Alkyl halides}}{R-X} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R-Mg-X}$

  (*ii*) **Wurtz reaction:**

  $R + X + 2Na + X - R \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R-R} + 2Na^+X^-$

ALCOHOLS

- Alkenes are converted to alcohol in different ways as follows

Reagent	Types of addition
dil H_2SO_4	Markovnikov
B_2H_6 and H_2O_2, OH^-	Anti-Markovnikov
Oxymercuration demercuration	– Markovnikov

- Oxidation of

  1° alcohol ⟶ aldehyde (with same no. of C atom) ⟶ carboxylic acid (with same no. of C atom)

  2° alcohol ⟶ ketone (with same no. of C atom) ⟶ carboxylic acid (with less no. of C atom)

  3° alcohol ⟶ ketone (with less no. of C atom) ⟶ carboxylic acid (with less no. of C atom)

PHENOLS

- Phenol $\xrightarrow{CHCl_3/OH^{\ominus}}$ Phenolic aldehyde (Reimer-Tieman reaction)
- Phenol $\xrightarrow[\Delta]{CO_2}$ Phenolic carboxylic acid (Kolbe's reaction)
- Acidity of phenols

  (i) Increases by electron withdrawing substituents like $-NO_2, -CN, -CHO, -COOH, -X, -\overset{+}{N}R_3$

  (ii) decreases by electron releasing substituents like $-R, -OH, -NH_2, -NR_2, -OR$

ETHERS

- $2ROH \xrightarrow[250°C]{Al_2O_3} R-O-R + H_2O$
- $RONa + X-R' \longrightarrow ROR' + NaX$ (Williamson's synthesis)
- $ROR + H_2O \xrightarrow[\Delta]{\text{dil. } H_2SO_4} 2ROH$

CARBONYL COMPOUNDS

- Formation of alcohols using RMgX

  (a) Formaldehyde + RMgX $\xrightarrow{\text{Hydrolysis}}$ 1° alcohol

  (b) Aldehyde + RMgX $\xrightarrow{\text{Hydrolysis}}$ 2° alcohol (other than HCHO)

  (c) Ketone + RMgX $\xrightarrow{\text{Hydrolysis}}$ 3° alcohol

- Cannizzaro reaction (Disproportionation)

  Aldehyde $\xrightarrow[\text{alkali}]{\text{Hot conc.}}$ Alcohol + Salt of acid

  (no α H-atom)
- Aldol condensation :

  Carbonyl compound + dil. alkali ⟶ β-hydroxy carbonyl compound

  (with α H-atom)
- Benzoin condensation

  Benzaldehyde $\xrightarrow[\text{NaCN}]{\text{ethanolic}}$ Benzoin
- The relative reactivities of different acid derivatives towards nucleophilic acyl substitution reaction follow the order:

$$\underset{\text{Acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} > \underset{\text{Anhydride}}{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R'} > \underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} > \underset{\text{Amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2}$$

CARBOXYLIC ACIDS

- The rate of esterfication decreases when alcohol, acid or both have branched substituents.
- Ortho effect : All ortho substituted benzoic acids (irrespective of type of substituent) are stronger than benzoic acid.

NITROGEN COMPOUNDS

- Order of basicity :

  ($R = -CH_3$ or $-C_2H_5$)

  $2° > 1° > 3° > NH_3$
- Hofmann degradation

  Amides $\xrightarrow{Br_2/KOH}$ 1° amine
- The basicity of amines is

  (i) decreased by electron withdrawing groups (ii) increased by electron releasing groups
- Reduction of nitrobenzene in different media gives different products

Medium	**Product**
Acidic	Aniline
Basic	Azoxy, Azo and finally hydrazobenzene
Neutral	Phenyl hydroxylamine

CARBOHYDRATES, AMINO ACIDS AND POLYMERS

- Carbohydrates are polyhydroxy aldehydes or ketones.
- Monosaccharides are simple sugars, containing three to nine carbon atoms.

- Characteristic reactions :

Homologous series	**Type of reactions**
(i) Alkanes	Substitution Mostly free radical
(ii) Alkenes and alkynes	Electrophillic addition
(iii) Arenes	Electrophillic substitution
(iv) Alkyl halides	Nucleophillic substitution
(v) Aldehyde and ketones	Nucleophillic addition

- Tests to differentiate :

1°, 2° and 3° alcohols	(i) Lucas test (ii) Victor meyer's test
1°, 2° and 3° amines	Hinsberg test
1°, 2° and 3° nitro compounds	Test with HNO_2 and KOH
Aryl halides and alkyl halides	Test with $AgNO_3$ solution
Aldehydes and ketones	Tollen's test/Fehling's test
Aromatic aldehydes and Aliphatic aldehydes	Fehling's test

IMPORTANT REAGENT

- Dil. H_2SO_4 [or Conc. $H_2SO_4 + H_2O$]

  Use → Hydrating agent (+HOH)
- Alc. KOH or $NaNH_2$(Use → -HX)

  $CH_3CH_2Cl \xrightarrow{\text{alc.KOH}} CH_2{=}CH_2$
- Lucas Reagent $ZnCl_2$ + Conc. HCl

  Use → For distinction between 1°, 2° & 3° alc.
- Tilden Reagent NOCl (Nitrosyl chloride)

  $C_2H_5NH_2 \xrightarrow{NOCl} C_2H_5Cl$
- Alkaline $KMnO_4$(Strong oxidant)

  Toluene → Benzoic acid
- Bayer's Reagent : 1% alkaline $KMnO_4$(Weak oxidant)

  Use: → For test of > C = C < or –C = C –

  $CH_2{=}CH_2 + H_2O + [O] \xrightarrow{BR} CH_2OH{-}CH_2OH$
- Acidic $K_2Cr_2O_7$ (Strong oxidant) : $RCH_2OH \xrightarrow{[O]} RCHO$
- $SnCl_2$/HCl or Sn/HCl used for reduction of nitrobenzene in acidic medium.

  $C_6H_5NO_2 \xrightarrow[6H]{SnCl_2/HCl} C_6H_5NH_2$
- Lindlar's Catalyst = $Pd/CaCO_3$

  + in small quantity $(CH_3COO)_2Pb$

  2 – butye + $H_2 \xrightarrow{''}$ Cis-2-butene (main product)
- Ziegler –Natta Catalyst $(C_2H_5)_3Al + TiCl_4$

  Use →In Addition polymerisation

IDENTIFICATION TESTS :

(i) Unsaturated compound (Bayer's reagent)
Decolourising the reagent

(ii) Alcohols (Ceric ammonium nitrate solution)
Red colouration

(iii) Phenols (Neutral $FeCl_3$ solution)
Violet/deep blue colouration

(iv) Aldehydes and ketones (2, 4-D.N.P.)
Orange precipitate

(v) Acids ($NaHCO_3$ solution)
Brisk effervescence (CO_2 is evolved)

(vi) 1° amine ($CHCl_3$ + KOH)
Foul smell (isocyanide)

(vii) 2° amine ($NaNO_2$ + HCl)
Yellow oily liquid (Nitrosoamine)