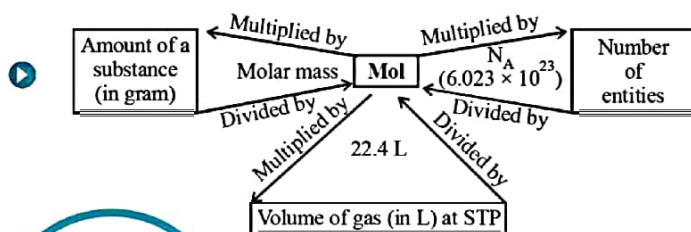


PHYSICAL CHEMISTRY



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

$$= \frac{\text{wt. of metal}}{\text{wt. of H}_2 \text{ displaced}} \times 1.008$$

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

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

 Molecular formula = (Empirical formula)_n

Energy of electron in species with one electron.

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

For energy in SI system,

$$E_n = \frac{-2\pi^2 m e^4 Z^2}{n^2 h^2 (4\pi\epsilon_0)^2}$$

$$E_n = \frac{-13.12 Z^2}{n^2} \text{ kJ mol}^{-1}$$

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

$$r = \frac{n^2 h^2}{4\pi^2 m Z e^2} = 0.529 \left(\frac{n^2}{Z} \right) \text{ \AA}$$

 Total energy of electron in the nth shell

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

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

$$E = hv = \frac{hc}{\lambda}$$

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

 No. of spectral lines produced when an electron drops from nth level to ground level = $\frac{n(n-1)}{2}$

 Heisenberg's Uncertainty Principle $(\Delta x)(\Delta p) \geq h/4\pi$

 Nodes $(n-1) = \text{total nodes}$, $\ell = \text{angular nodes}$, $(n-\ell-1) = \text{Radial nodes}$

 Orbital angular momentum : $\sqrt{\ell(\ell+1)} \frac{h}{2\pi} = \sqrt{\ell(\ell+1)} h$

(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.

CHEMICAL BONDING

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

$$= [\text{total number of valence electrons in the free atoms}] - [\text{total number of non-binding (lone pair) electrons}]$$

$$- \frac{1}{2} [\text{total number of bonding (shared) electrons}]$$

 Relative bond strength : $sp^3d^2 > dsp^2 > sp^3 > sp^2 > sp > p-p$ (Co-axial) $> s-p > s-s > p-p$ (Co-lateral)

▶ **VSEPR theory**

- (i) (LP-LP) repulsion > (LP-BP) > (BP-BP)
- (ii) $\text{NH}_3 \rightarrow$ Bond Angle $106^\circ 45'$ because (LP-BP) repulsion > (BP-BP) $\text{H}_2\text{O} \rightarrow 104^\circ 27'$ because (LP-LP) repulsion > (LP-LB) > (BP-BP)

▶ **Hybridisation :**

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

CHEMICAL EQUILIBRIUM

▶ $K_p = K_c (RT)^{\Delta n_g}$ where $\Delta n_g = n_p - n_r$

▶ **Free Energy Change (ΔG)**

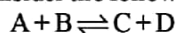
- (a) If $\Delta G = 0$ then reversible reaction would be in equilibrium, $K_c = 0$
- (b) If $\Delta G = (+)$ ve then equilibrium will be displaced in backward direction; $K_c < 1$

(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



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

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.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

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

$$\Delta G^\circ = -RT \ln K_c$$

$$\therefore \Delta G^\circ = -RT \ln K_p$$

- ▶ **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 EQUILIBRIUM

- ▶ (i) Lewis Acid (e^- pair acceptor) \rightarrow $\text{CO}_2, \text{BF}_3, \text{AlCl}_3, \text{ZnCl}_2$, normal cation

- (ii) Lewis Base (e^- pair donor) \rightarrow $\text{NH}_3, \text{ROH}, \text{ROR}, \text{H}_2\text{O}, \text{RNH}_2$, normal anions

▶ **Dissociation of Weak Acid and Weak Base**

- (i) Weak Acid, $K_a = Cx^2/(1-x)$ or $K_a = Cx^2$; $x \ll 1$
- (ii) Weak Base, $K_b = Cx^2/(1-x)$ or $K_b = Cx^2$; $x \ll 1$

- ▶ Buffer solution {Henderson equation} :

(i) Acidic, $\text{pH} = \text{p}K_a + \log \{\text{Salt}/\text{Acid}\}$.
For maximum buffer action $\text{pH} = \text{p}K_a$
Range of buffer $\text{pH} = \text{p}K_a \pm 1$

(ii) Alkaline \rightarrow $\text{pOH} = \text{p}K_b + \log \{\text{Salt}/\text{Base}\}$ for max. buffer action $\text{pH} = 14 - \text{p}K_b$
Range $\text{pH} = 14 - \text{p}K_b \pm 1$

(iii) Buffer Capacity = $\frac{\text{Moles / lit of Acid or Base Mixed}}{\text{Change in pH}}$

- ▶ Relation between ionisation constant (K_i) and degree of ionisation (α):-

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

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

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

- ▶ **Common ion effect :** By addition of X mole/L of a common ion, to a weak acid (or weak base) α becomes equal to

$$\frac{K_a}{X} \left(\text{or } \frac{K_b}{X} \right) \quad [\text{where } \alpha = \text{degree of dissociation}]$$

- ▶ (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 :

$$\text{pH} = 0.5 (\text{p}K_w + \text{p}K_a + \log c); \quad h = \sqrt{\frac{K_h}{c}}; \quad K_h = \frac{K_w}{K_a}$$

(h = degree of hydrolysis)

Salt of weak base and strong acid :

$$\text{pH} = 0.5 (\text{p}K_w - \text{p}K_b - \log c); \quad h = \sqrt{\frac{K_w}{K_b \times c}}$$

Salt of weak acid and weak base :

$$\text{pH} = 0.5 (\text{p}K_w + \text{p}K_a - \text{p}K_b); \quad h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

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 :**

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \quad \& \quad t_{1/2} = \frac{0.693}{k}$$

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

- ▶ **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 -

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

REVISION CAPSULE - CHEMISTRY

- ▶ **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 n^{th} 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 = $\frac{[A]_0}{2^n}$

- ▶ **Arrhenius equation** : $k = Ae^{-E_a/RT}$, slope = $\frac{-E_a}{2.303R}$
and Temperature Coefficient

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

- ▶ 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 $1/\text{O.N}$
- ▶ (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 \uparrow
- (b) Standard Oxidation Potential \downarrow
- (c) Reducing Capacity \downarrow
- (d) IP \uparrow

(e) Reactivity \downarrow

THERMODYNAMICS

- ▶ First Law of Thermodynamics :

$$\Delta E = Q + W$$

Expression for pressure volume work

$$W = -P\Delta V$$

Maximum work in a reversible expansion :

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

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

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

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

Enthalpy 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

$$\Delta S = \sum S_p - \sum S_R$$

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

- ▶ Free energy change : $\Delta G = \Delta H - T\Delta S$, $\Delta G^\circ = -nFE^\circ_{\text{cell}}$

$$-\Delta G = W(\text{maximum}) - P\Delta V, \Delta G_{\text{system}} = -T\Delta S_{\text{total}}$$

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

$$m = Z \cdot I \cdot t$$

$$\text{Degree of dissociation} : \alpha = \frac{\lambda_{\text{eq}}}{\lambda_{\text{eq}}^0}$$

- ▶ Specific conductance

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

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

- ▶ Kohlrausch's law : $\Lambda_m^0 = x\lambda_A^0 + y\lambda_B^0$

- ▶ Nernst Equation

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

$$\& E^\circ_{\text{cell}} = E^\circ_{\text{right}} + E^\circ_{\text{left}} \& K_{\text{eq}} = \text{antilog} \left[\frac{nE^\circ}{0.0591} \right]$$

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

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

- ▶ Calculation of pH of an electrolyte by using a calomel electrode :

$$\text{pH} = \frac{E_{\text{cell}} - 0.2415}{0.0591}$$

- ▶ Thermodynamic efficiency of fuel cells :

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

For $\text{H}_2\text{-O}_2$ fuel cells it is 95%.

- ▶ $P = K_H \cdot x$

- ▶ 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
 $P = p_A + p_B = p_A^o X_A + p_B^o X_B$
- ▶ Characteristics of an ideal solution:
 (i) $\Delta_{sol}V = 0$ (ii) $\Delta_{sol}H = 0$
- ▶ Relative lowering of vapour pressure

$$\frac{P_A^o - P_A}{P_A^o} = \frac{n_B}{n_A + n_B}$$

- ▶ 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

$$\Delta T_b = \frac{1000 K_b}{M_1} \left(\frac{p^o - p}{p^o} \right) \quad (M_1 = \text{mol. wt. of solvent})$$

- ▶ Osmotic pressure (P) with depression in freezing point ΔT_f

$$P = \Delta T_f \times \frac{dRT}{1000 K_f}$$

- ▶ 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) $\pi = \Delta T_b \times \frac{dRT}{1000 K_b}$ Elevation in boiling point

(iii) $\pi = \Delta T_f \times \frac{dRT}{1000 K_f}$ 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) $R = 0.0821 \text{ liter atm. deg}^{-1} \text{ mole}^{-1}$
 (ii) $R = 2 \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 (iii) $R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$
- ▶ Velocities related to gaseous state

$$\text{RMS velocity} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

$$\text{Average speed} = \sqrt{\frac{8RT}{M}} \quad \& \quad \text{Most probable speed} = \sqrt{\frac{2RT}{M}}$$

Average speed = $0.9213 \times$ RMS speed
 RMS speed = $1.085 \times$ Average speed
 MPS = $.816 \times$ 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

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \quad \text{for } n \text{ moles}$$

▶ 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 [$\uparrow\uparrow\uparrow\uparrow$]

- ▶ Antiferromagnetic : Net magnetic moment is zero [$\uparrow\downarrow\uparrow\downarrow$]

- ▶ Ferrimagnetic : Net magnetic moment is three [$\uparrow\downarrow\downarrow\uparrow\uparrow$]

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 , $\text{Fe}(\text{OH})_3$ sol]

- ▶ Preparation of colloidal solution :

(i) Dispersion methods (ii) Condensation method.

▶ Coagulating power $\propto \frac{1}{\text{Flocculating value}}$

- ▶ Properties of colloidal solution :

(i) Tyndall effect (ii) Brownian movement
 (iii) Coagulation (iv) Filtrability.

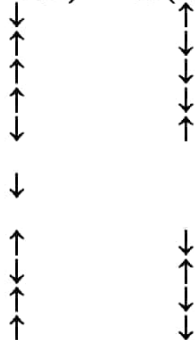
INORGANIC CHEMISTRY

PERIODIC TABLE

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

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



$$IP \propto \frac{1}{\text{Metallic character}} \propto \frac{1}{\text{Reducing character}}$$

$$EA \propto \frac{1}{\text{size}} \propto \text{nuclear charge.}$$

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 $Li - \text{Red, Na - Golden, K - Violet, Rb - Red, Cs - Blue, Ca - Brick red, Sr - Blood red, Ba - Apple green}$

- 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) $SO < SO_2 < SO_3$; $SO_2 > TeO_2 > SeO_2 > PoO_2$

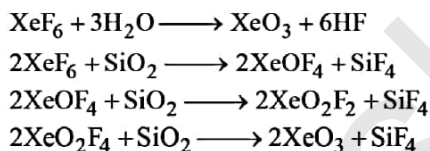
HALOGEN FAMILY

- ▶ Bond energy of halogens : $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$
- ▶ Solubility of halogen in water : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- ▶ Oxidising power : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- ▶ Enthalpy of hydration of X^- ion : $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

- ▶ Reactivity of halogens : $\text{F} > \text{Cl} > \text{Br} > \text{I}$
- ▶ Ionic character of M - X bond in halides
 $\text{M}-\text{F} > \text{M}-\text{Cl} > \text{M}-\text{Br} > \text{M}-\text{I}$
- ▶ Reducing character of X^- ion : $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$
- ▶ Acidic strength of halogen acids : $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
- ▶ Conjugate base strength of halogen acids
 $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$
- ▶ Reducing property of hydrogen halides
 $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$
- ▶ Oxidising power of oxides of chlorine
 $\text{Cl}_2\text{O} > \text{ClO}_2 > \text{Cl}_2\text{O}_6 > \text{Cl}_2\text{O}_7$
- ▶ Acidic character of oxyacids of chlorine
 $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
- ▶ Oxidising power of oxyacids of chlorine
 $\text{HClO} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$

NOBLE GASES

- ▶ $\text{XeF}_2 + \text{PF}_5 \longrightarrow [\text{XeF}]^+ [\text{PF}_6]^-$
- ▶ $\text{XeF}_4 + \text{SbF}_5 \longrightarrow [\text{XeF}_3]^+ [\text{SbF}_6]^-$
- ▶ $\text{XeF}_6 + \text{H}_2\text{O} \longrightarrow \text{XeOF}_4 + 2\text{HF}$
- ▶ $\text{XeF}_6 + 2\text{H}_2\text{O} \longrightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$
- ▶ $2\text{XeF}_4 + 3\text{H}_2\text{O} \longrightarrow \text{Xe} + \text{XeO}_3 + 4\text{HF} + \text{F}_2$



TRANSITION ELEMENTS (d- and f-BLOCK ELEMENTS)

- ▶ The element with exceptional configuration are
 $\text{Cr}^{24}[\text{Ar}] 3d^5 4s^1$, $\text{Cu}^{29}[\text{Ar}] 3d^{10} 4s^1$
 $\text{Mo}^{42}[\text{Kr}] 4d^5 5s^1$, $\text{Pd}^{46}[\text{Kr}] 4d^{10} 5s^0$
 $\text{Ag}^{47}[\text{Kr}] 4d^{10} 5s^1$, $\text{Pt}^{78}[\text{Xe}] 4f^{14} 5d^{10} 6s^0$
- ▶ Inner Transition Elements
- (i) Electronic Configuration -
 $[\text{Xe}] 4f^{0-14} 5d^{0-1} 6s^2$

- (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
 $= (\text{Z} - \text{Oxidation number}) + (2 \times \text{Coordination number})$
- ▶ 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 ; MABX_2
 - (2) Octahedral of the type : MA_4XY , MA_4X_2 , MA_3X_3 , $\text{MA}_2\text{X}_2\text{Y}_2$, $\text{M}(\text{AA})_2\text{X}_2$ and $\text{M}(\text{ABCDE})\text{F}$.
 - (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 \rightarrow Free radicals
Heterolytic fission \rightarrow 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.

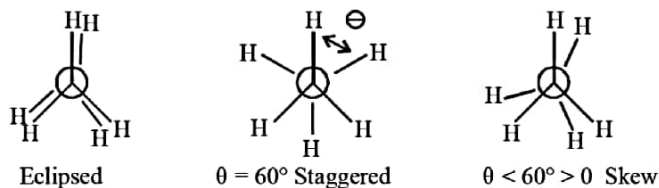
Two types : (i) Cations (ii) Neutral molecules with vacant orbitals (Lewis acids).

- ▶ 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.

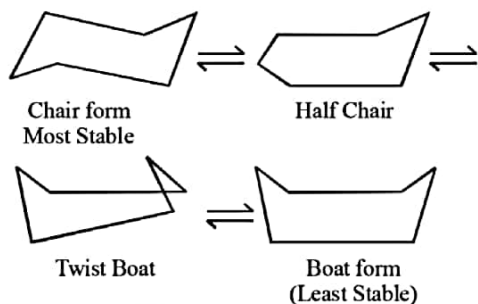
ALKANES

- ▶ 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 $3^\circ > 2^\circ > 1^\circ$ (Saytzeff's rule).

The lower the ΔH_h (heat of hydrogenation) the more stable the alkene is.

Alkenes undergo anti-Markovnikov addition only with HBr in the presence of peroxides.

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.

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

They are : -OH, -NH₂, -X, -R, -OR, etc.

All m-directing groups are ring deactivating groups.

They are : -CHO, -COOH, -NO₂, -CN, -NR₃, etc.

ARENES

The order of reactivity is

(i) RI > RBr > RCl > RF

(i) Allyl halide > Alkyl halide > Vinyl halide

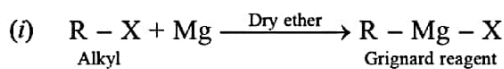
(iii) Alkyl halide > Aryl halide

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.

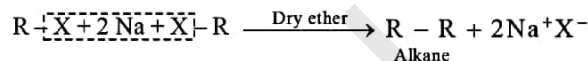
HALOGEN COMPOUNDS

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:



(ii) **Wurtz reaction:**

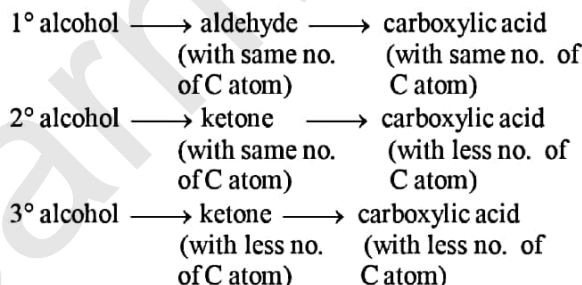


ALCOHOLS

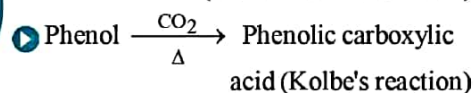
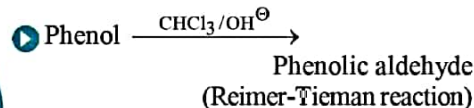
Alkenes are converted to alcohol in different ways as follows

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

Oxidation of



PHENOLS



Acidity of phenols

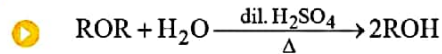
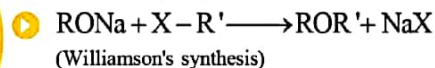
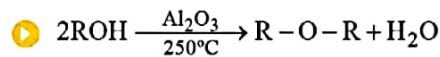
(i) Increases by electron withdrawing substituents like

-NO₂, -CN, -CHO, -COOH, -X, -NR₃⁺

(ii) decreases by electron releasing substituents like

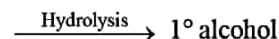
-R, -OH, -NH₂, -NR₂, -

OR



Formation of alcohols using RMgX

(a) Formaldehyde + RMgX



2° alcohol

(other than HCHO)



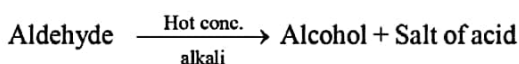
3° alcohol

ETHERS

CARBONYL COMPOUNDS

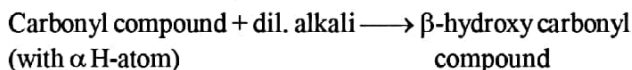
REVISION CAPSULE - CHEMISTRY

▶ Cannizzaro reaction (Disproportionation)

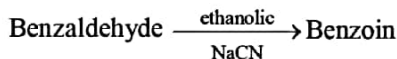


(no α -H-atom)

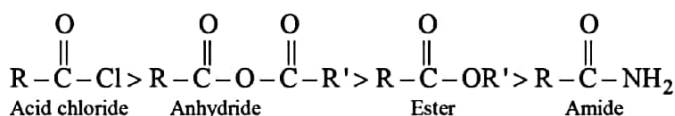
▶ Aldol condensation :



▶ Benzoin condensation



▶ The relative reactivities of different acid derivatives towards nucleophilic acyl substitution reaction follow the order:



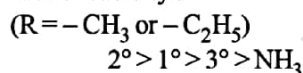
CARBOXYLIC ACIDS

▶ The rate of esterification 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 :



▶ Hofmann degradation



▶ 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

- Alkanes
- Alkenes and alkynes
- Arenes
- Alkyl halides
- Aldehyde and ketones

Type of reactions

- Substitution
Mostly free radical
Electrophilic addition
Electrophilic substitution
Nucleophilic substitution
Nucleophilic 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. H₂SO₄ [or Conc. H₂SO₄ + H₂O]
Use → Hydrating agent (+HOH)
- ▶ Alc. KOH or NaNH₂ (Use → -HX)
CH₃CH₂Cl $\xrightarrow{\text{alc. KOH}}$ CH₂=CH₂
- ▶ Lucas Reagent ZnCl₂ + Conc. HCl
Use → For distinction between 1°, 2° & 3° alc.

▶ Tilden Reagent NOCl (Nitrosyl chloride)

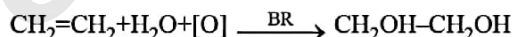


▶ Alkaline KMnO₄ (Strong oxidant)

Toluene → Benzoic acid

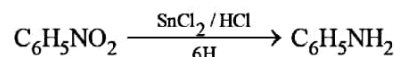
▶ Bayer's Reagent : 1% alkaline KMnO₄ (Weak oxidant)

Use: → For test of >C=C< or -C=C-



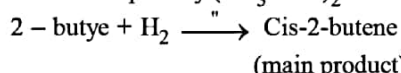
▶ Acidic K₂Cr₂O₇ (Strong oxidant) : RCH₂OH $\xrightarrow{[\text{O}]}$ RCHO

▶ SnCl₂/HCl or Sn/HCl used for reduction of nitrobenzene in acidic medium.



▶ Lindlar's Catalyst = Pd/CaCO₃

+ in small quantity (CH₃COO)₂Pb



▶ Ziegler-Natta Catalyst (C₂H₅)₃Al + TiCl₄

Use → In Addition polymerisation

IDENTIFICATION TESTS :

- Unsaturated compound (Bayer's reagent)
Decolourising the reagent
- Alcohols (Ceric ammonium nitrate solution)
Red colouration
- Phenols (Neutral FeCl₃ solution)
Violet/deep blue colouration
- Aldehydes and ketones (2, 4-D.N.P.)
Orange precipitate
- Acids (NaHCO₃ solution)
Brisk effervescence (CO₂ is evolved)
- 1° amine (CHCl₃ + KOH)
Foul smell (isocyanide)
- 2° amine (NaNO₂ + HCl)
Yellow oily liquid (Nitrosoamine)