



# Chemistry

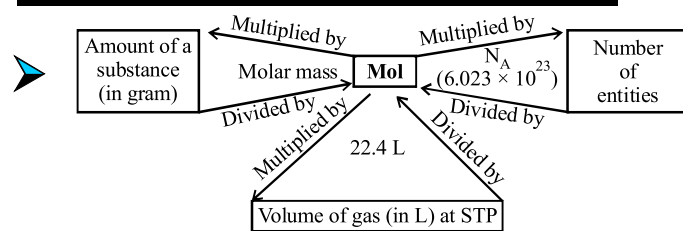
# Formulae Book

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## 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 =  $2 \times \text{VD}$
- 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 = (Empirical formula)<sub>n</sub>

### 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,  $E_n = \frac{-2\pi^2 me^4 Z^2}{n^2 h^2 (4\pi\epsilon_0)^2}$   

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

$$mvr = \frac{nh}{2\pi}$$
- $$r = \frac{n^2 h^2}{4\pi^2 mZe^2} = 0.529 \left( \frac{n^2}{Z} \right) \text{ \AA}$$
- Total energy of electron in the n<sup>th</sup> shell  

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

- $$\bar{\nu} = \frac{1}{\lambda} = RZ^2 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right], [R = 1.0968 \times 10^7 \text{ m}^{-1}]$$
- $$E = h\nu = \frac{hc}{\lambda}, \lambda = \frac{h}{\sqrt{2m \times \text{K.E.}}}$$
- No. of spectral lines produced when an electron drops from n<sup>th</sup> 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,  $\ell$  = angular nodes,  $(n-\ell-1)$  = Radial nodes
- Orbital angular momentum :  $\sqrt{\ell(\ell+1)} \frac{h}{2\pi} = \sqrt{\ell(\ell+1)} \hbar$

### 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.  $\text{Cu}^+, \text{Ag}^+, \text{Zn}^{2+}, \text{Cd}^{2+}$
- 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 :**  $sp^3 d^2 > dsp^2 > sp^3 > sp^2 > sp > p-p$  (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  $107^\circ 45'$  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 ( $\Delta G$ )
  - (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  $\rightarrow (\text{mol/lit})^{\Delta n}$ ,  
(b)  $K_p$  unit  $\rightarrow (\text{atm})^{\Delta n}$
- **Reaction Quotient and Equilibrium Constant**

Consider the following reversible reaction  $A + B \rightleftharpoons C + D$

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

**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  $\text{pH} = 14 - \text{p}K_b \pm 1$

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

- Relation between ionisation constant ( $K_i$ ) and degree of ionisation ( $\alpha$ ) : -  $K_i = \frac{\alpha^2}{(1-\alpha)V} = \frac{\alpha^2 C}{(1-\alpha)}$  (Ostwald's dilution law)  
It is applicable to weak electrolytes for which  $\alpha \ll 1$  then

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

- **Common ion effect :** By addition of X mole/L of a common ion, to a weak acid (or weak base)  $\alpha$  becomes equal to  $\frac{K_a}{X}$  (or  $\frac{K_b}{X}$ ) [where  $\alpha$  = 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 :

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

(h = degree of hydrolysis)

Salt of weak base and strong acid :

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

Salt of weak acid and weak base :

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

## 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 :**

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \text{ \& } t_{1/2} = \frac{0.693}{k} [A]_t = [A]_0 e^{-kt}$$

- **Second Order Reactions :** When concentration of A and B

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

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  $n^{\text{th}}$  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  $10^\circ\text{C}$ , the rate constant gets nearly doubled.

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

## REDOX REACTIONS

- Oxidant itself is reduced (gives  $\text{O}_2$ )  
Or Oxidant  $\longrightarrow e^-$  (s) Acceptor  
Reductant itself is oxidised (gives  $\text{H}_2$ )  
Or reductant  $\longrightarrow e^-$  (s) Donor
- (i) Strength of acid  $\propto \text{O.N}$   
(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,  $\text{H}_2$ , Cu, Ag, Pt, Au.  
(ii) As we move from top to bottom in this series  
(a) Standard Reduction Potential  $\uparrow$   
(b) Standard Oxidation Potential  
(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 :  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta G^\circ = -nFE^\circ_{\text{cell}}$   
 $-\Delta G = W(\text{maximum}) - P\Delta V$ ,  $\Delta G_{\text{system}} = -T\Delta S_{\text{total}}$

$\Delta H$	$\Delta S$	$\Delta G$	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.

## ELECTROCHEMISTRY

- $m = Z.I.t$

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

- Specific conductance

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

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

- 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) =  $\frac{\text{number of moles}}{\text{volume of the solution in litres}}$

## SOLUTIONS

- Raoult's law

$$P = p_A + p_B = p^\circ_A X_A + p^\circ_B X_B$$

- **Characteristics of an ideal solution:**

(i)  $\Delta_{\text{sol}} V = 0$  (ii)  $\Delta_{\text{sol}} H = 0$



➤ 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  $\Delta T_f$

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

➤ 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)  $R = 0.0821 \text{ liter atm. deg}^{-1} \text{ mole}^{-1}$

(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

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

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

$$\text{Average speed} = 0.9213 \times \text{RMS speed}$$

$$\text{RMS speed} = 1.085 \times \text{Average speed}$$

$$\text{MPS} = .816 \times \text{RMS}; \text{RMS} = 1.224 \text{ MPS}$$

$$\text{MPS} : \text{A.V. speed} : \text{RMS} = 1 : 1.128 : 1.224$$

➤ 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 STATE

➤ Available space filled up by hard spheres (packing fraction):

$$\text{Simple cubic} = \frac{\pi}{6} = 0.52$$

$$bcc = \frac{\pi\sqrt{3}}{8} = 0.68; fcc = \frac{\pi\sqrt{2}}{6} = 0.74; hcp = \frac{\pi\sqrt{2}}{6} = 0.74$$

$$\text{diamond} = \frac{\pi\sqrt{3}}{6} = 0.34$$

➤ 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 :

$$\text{Simple cubic} = r = \frac{a}{2}; bcc \ r = \frac{\sqrt{3}a}{4}; fcc \ r = \frac{\sqrt{2}a}{4}$$

➤ 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 [ $\uparrow\downarrow\uparrow\downarrow$ ]

## SURFACE CHEMISTRY

➤ **Ferrimagnetic** : Net magnetic moment is three [ $\uparrow\downarrow\downarrow\uparrow$ ]

➤ **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.  $\text{As}_2\text{S}_3$ ,  $\text{Fe}(\text{OH})_3$  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 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	↑	↓

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

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

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 - 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  $\text{X}^-$  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  $\text{X}^-$  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

## NOBLE GASES

- $\text{HClO} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$
- $\text{XeF}_2 + \text{PF}_5 \longrightarrow [\text{XeF}]^+ [\text{PF}_6]^-$
- $\text{XeF}_4 + \text{SbF}_5 \longrightarrow [\text{XeF}_3]^+ [\text{SbF}_6]^-$
- $\text{XeF}_6 + \text{H}_2\text{O} \longrightarrow \text{XeOF}_4 + 2\text{HF}$
- $\text{XeF}_6 + 2\text{H}_2\text{O} \longrightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$
- $2\text{XeF}_4 + 3\text{H}_2\text{O} \longrightarrow \text{Xe} + \text{XeO}_3 + 4\text{HF} + \text{F}_2$
- $\text{XeF}_6 + 3\text{H}_2\text{O} \longrightarrow \text{XeO}_3 + 6\text{HF}$
- $2\text{XeF}_6 + \text{SiO}_2 \longrightarrow 2\text{XeOF}_4 + \text{SiF}_4$
- $2\text{XeOF}_4 + \text{SiO}_2 \longrightarrow 2\text{XeO}_2\text{F}_2 + \text{SiF}_4$
- $2\text{XeO}_2\text{F}_4 + \text{SiO}_2 \longrightarrow 2\text{XeO}_3 + \text{SiF}_4$

## 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**
  - Electronic Configuration** -  $[\text{Xe}] 4f^{0-14} 5d^{0-1} 6s^2$
  - 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  
 $= (Z - \text{Oxidation number}) + (2 \times \text{Coordination number})$
- Factors affecting stability of complex
  - Greater the charge on the central metal ion, greater is the stability.
  - Greater the ability of the ligand to donate electron pair (basic strength) greater is the stability.
  - Formation of chelate rings increases the stability.
- Isomerism in coordination compounds :
  - Structural Isomerism
  - Ionization Isomerism
  - Hydration Isomerism
  - Linkage Isomerism
  - Polymerisation Isomerism
  - Valence Isomerism
  - Coordination Position Isomerism
  - Stereo Isomerism
    - Geometrical Isomerism*
      - Square planar complexes of the type  $\text{MA}_2\text{X}_2$ ;  $\text{MABX}_2$ ;  $\text{MABXY}$
      - Octahedral of the type :  $\text{MA}_4\text{XY}$ ,  $\text{MA}_4\text{X}_2$ ,  $\text{MA}_3\text{X}_3$ ,  $\text{MA}_2\text{X}_2\text{Y}_2$ ,  $\text{M}(\text{AA})_2\text{X}_2$  and  $\text{M}(\text{ABCDEF})$ .
    - Optical isomerism*

# ORGANIC CHEMISTRY

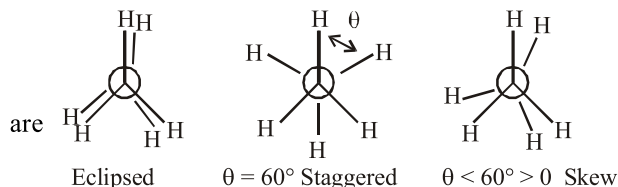
## GENERAL ORGANIC CHEMISTRY

- 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

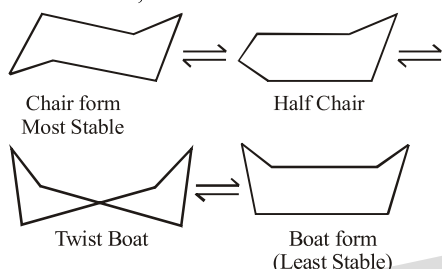
- Heterolytic fission  $\rightarrow$  Ions (Carbonium ions, carbanions etc.)
- Nucleophiles – Electron rich  
 Two types : (i) Anions (ii) Neutral molecules with lone pair of electrons (Lewis bases)
- Electrophiles : Electron deficient.  
 Two types : (i) Cations (ii) Neutral molecules with vacant orbitals (Lewis acids).
- Inductive effect is due to  $\sigma$  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



- 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  $\Delta H_h$  (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<sub>2</sub>, -X, -R, -OR, etc.
- All m-directing groups are ring deactivating groups. They are : -CHO, -COOH, -NO<sub>2</sub>, -CN, - $\overset{+}{N}R_3$ , etc.

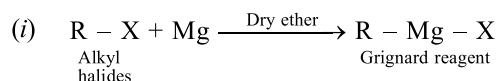
## HALOGEN COMPOUNDS

- The order of reactivity is
  - $RI > RBr > RCl > RF$
  - Allyl halide > Alkyl halide > Vinyl halide
  - Alkyl halide > Aryl halide

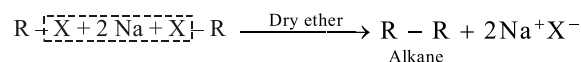
- $S_N1$  reaction :** Mainly  $3^\circ$  alkyl halides undergo this reaction and form racemic mixture.  $S_N1$  is favoured by polar solvent and low concentration of nucleophile.

- $S_N2$  reaction :** Mainly  $1^\circ$  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	Types of addition
dil $H_2SO_4$	Markovnikov
$B_2H_6$ and $H_2O_2$ , $OH^-$	Anti-Markovnikov
Oxymercuration demercuration	Markovnikov

- Oxidation of

$1^\circ$ alcohol	→ aldehyde	→ carboxylic acid
	(with same no. of C atom)	(with same no. of C atom)
$2^\circ$ alcohol	→ ketone	→ carboxylic acid
	(with same no. of C atom)	(with less no. of C atom)
$3^\circ$ alcohol	→ ketone	→ carboxylic acid
	(with less no. of C atom)	(with less no. of C atom)

## PHENOLS

- Phenol  $\xrightarrow{CHCl_3/OH^-}$  Phenolic aldehyde (Reimer-Tieman reaction)
- Phenol  $\xrightarrow{CO_2, \Delta}$  Phenolic carboxylic acid (Kolbe's reaction)
- Acidity of phenols
  - Increases by electron withdrawing substituents like -NO<sub>2</sub>, -CN, -CHO, -COOH, -X, - $\overset{+}{N}R_3$
  - decreases by electron releasing substituents like -R, -OH, -NH<sub>2</sub>, -NR<sub>2</sub>, -OR

## ETHERS

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

## CARBONYL COMPOUNDS

- Formation of alcohols using  $RMgX$ 
  - Formaldehyde +  $RMgX \xrightarrow{\text{Hydrolysis}} 1^\circ$  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

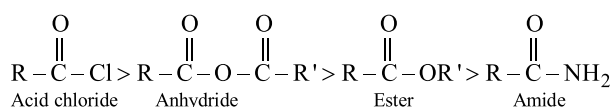
(no  $\alpha$  H-atom)

➤ Aldol condensation :

Carbonyl compound + dil. alkali  $\longrightarrow$   $\beta$ -hydroxy carbonyl compound  
(with  $\alpha$  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:



## 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 :

(R =  $-\text{CH}_3$  or  $-\text{C}_2\text{H}_5$ )  $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$

➤ Hofmann degradation

Amides  $\xrightarrow{\text{Br}_2/\text{KOH}}$  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

## BIOMOLECULES

➤ Carbohydrates are polyhydroxy aldehydes or ketones.

➤ Monosaccharides are simple sugars, containing three to nine carbon atoms.

➤ Characteristic reactions :

**Homologous series**

(i) Alkanes

(ii) Alkenes and alkynes

(iii) Arenes

(iv) Alkyl halides

(v) 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  $\text{HNO}_2$  and KOH

Aryl halides and alkyl halides Test with  $\text{AgNO}_3$  solution

Aldehydes and ketones Tollen's test/Fehling's test

Aromatic aldehydes and Fehling's test

Aliphatic aldehydes

## IMPORTANT REAGENTS

➤ Dil.  $\text{H}_2\text{SO}_4$  [or Conc.  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ ]

Use  $\rightarrow$  Hydrating agent (+HOH)

➤ Alc. KOH or  $\text{NaNH}_2$  (Use  $\rightarrow -\text{HX}$ )

$\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{alc. KOH}} \text{CH}_2=\text{CH}_2$

➤ Lucas Reagent  $\text{ZnCl}_2 + \text{Conc. HCl}$

Use  $\rightarrow$  For distinction between 1°, 2° & 3° alc.

➤ Tilden Reagent  $\text{NOCl}$  (Nitrosyl chloride)

$\text{C}_2\text{H}_5\text{NH}_2 \xrightarrow{\text{NOCl}} \text{C}_2\text{H}_5\text{Cl}$

➤ Alkaline  $\text{KMnO}_4$  (Strong oxidant)

Toluene  $\rightarrow$  Benzoic acid

➤ Bayer's Reagent : 1% alkaline  $\text{KMnO}_4$  (Weak oxidant)

Use:  $\rightarrow$  For test of  $> \text{C} = \text{C} <$  or  $-\text{C} = \text{C} -$

$\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} + [\text{O}] \xrightarrow{\text{BR}} \text{CH}_2\text{OH}-\text{CH}_2\text{OH}$

➤ Acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  (Strong oxidant) :  $\text{RCH}_2\text{OH} \xrightarrow{[\text{O}]} \text{RCHO}$

➤  $\text{SnCl}_2/\text{HCl}$  or  $\text{Sn}/\text{HCl}$  used for reduction of nitrobenzene in

acidic medium.  $\text{C}_6\text{H}_5\text{NO}_2 \xrightarrow[6\text{H}]{\text{SnCl}_2/\text{HCl}} \text{C}_6\text{H}_5\text{NH}_2$

➤ Lindlar's Catalyst =  $\text{Pd}/\text{CaCO}_3$  + in small quantity

$(\text{CH}_3\text{COO})_2\text{Pb} + 2 \text{ butyne} \xrightarrow{\text{H}_2} \text{Cis-2-butene}$   
(main product)

➤ Ziegler-Natta Catalyst  $(\text{C}_2\text{H}_5)_3\text{Al} + \text{TiCl}_4$

Use  $\rightarrow$  In Addition polymerisation

## IDENTIFICATION TESTS

➤ Unsaturated compound (Bayer's reagent)

Decolourising the reagent

➤ Alcohols (Ceric ammonium nitrate solution)

Red colouration

➤ Phenols (Neutral  $\text{FeCl}_3$  solution)

Violet/deep blue colouration

➤ Aldehydes and ketones (2, 4-D.N.P.)

Orange precipitate

➤ Acids ( $\text{NaHCO}_3$  solution)

Brisk effervescence ( $\text{CO}_2$  is evolved)

➤ 1° amine ( $\text{CHCl}_3 + \text{KOH}$ )

Foul smell (isocyanide)

➤ 2° amine ( $\text{NaNO}_2 + \text{HCl}$ )

Yellow oily liquid (Nitrosoamine)

“

**Do not go  
where the  
path may **lead,**  
go instead where there  
is no path and  
**leave a trail.****



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