

Physical Chemistry

Some Basic Concepts of Chemistry

- Atomic mass = $\frac{\text{Average mass of an atom}}{\frac{1}{12} \times \text{Mass of an atom of C-12}}$
- Number of gram atoms = $\frac{\text{Mass of an element}}{\text{Gram atomic mass}}$
- Atomic mass = 6.4/Specific heat (cal/g)
- Mass per cent (%) = $\frac{w_{\text{solute}}}{w_{\text{solution}}} \times 100$
- Mole fraction (x_A) = $\frac{n_A}{n_A + n_B}$, (x_B) = $\frac{n_B}{n_A + n_B}$
- Molarity (M) = $\frac{w_2 \times 1000}{M_2 \times V(\text{in mL})}$
- Molality (m) = $\frac{w_2 \times 1000}{M_2 \times w_1(\text{in g})}$

Structure of Atom

- $E = h\nu = \frac{hc}{\lambda}$; $\frac{1}{\lambda} = \bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1}$;
- $mvr = \frac{nh}{2\pi}$; $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$
- $r_n = \frac{n^2}{Z} \times 0.529 \text{ \AA}$; $E_n = \frac{-Z^2}{n^2} \times 13.6 \text{ eV/atom}$
- $v_n = \frac{Z}{n} \times 2.188 \times 10^8 \text{ cm/s}$;
- $K.E. = \frac{1}{2} \frac{kZe^2}{r}$; $P.E. = \frac{-kZe^2}{r_n}$

Thermodynamics

- $\Delta U = q + w$
- $w_{\text{irr}} = -P\Delta V$
- $w_{\text{rev}} = -2.303nRT \log \frac{V_2}{V_1} = -2.303nRT \log \frac{P_1}{P_2}$
- $\Delta H = \Delta E + \Delta n_g RT$; $C_v = \left(\frac{\partial E}{\partial T} \right)_V$; $C_p = \left(\frac{\partial H}{\partial T} \right)_P$
- $\log \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$
- $\Delta S = 2.303nR \log \left(\frac{V_2}{V_1} \right)$; $\Delta G = \Delta H - T\Delta S$
- $\Delta G^\circ = -2.303 RT \log K$, $\Delta G^\circ = -nFE_{\text{cell}}^\circ$

States of Matter

- $P_1 V_1 = P_2 V_2$; $\frac{V_1}{T_1} = \frac{V_2}{T_2}$; $\frac{P_1}{T_1} = \frac{P_2}{T_2}$; $\frac{V_1}{n_1} = \frac{V_2}{n_2}$; $PV = nRT$
- $d = \frac{PM}{RT}$; $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}} = \frac{v_1 t_2}{v_2 t_1}$; $K.E. = \frac{3}{2} kT$
- $c_{\text{rms}} = \sqrt{3RT/M}$; $c_{\text{mp}} = \sqrt{2RT/M}$; $c_{\text{av}} = \sqrt{8RT/\pi M}$
- $T_b = a/Rb$; $T_c = 8a/27Rb$; $P_c = a/27b^2$; $V_c = 3b$
- $Z = \frac{PV_m}{nRT}$; $P_c V_c = \frac{3}{8} RT_c$; $\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$

Equilibrium

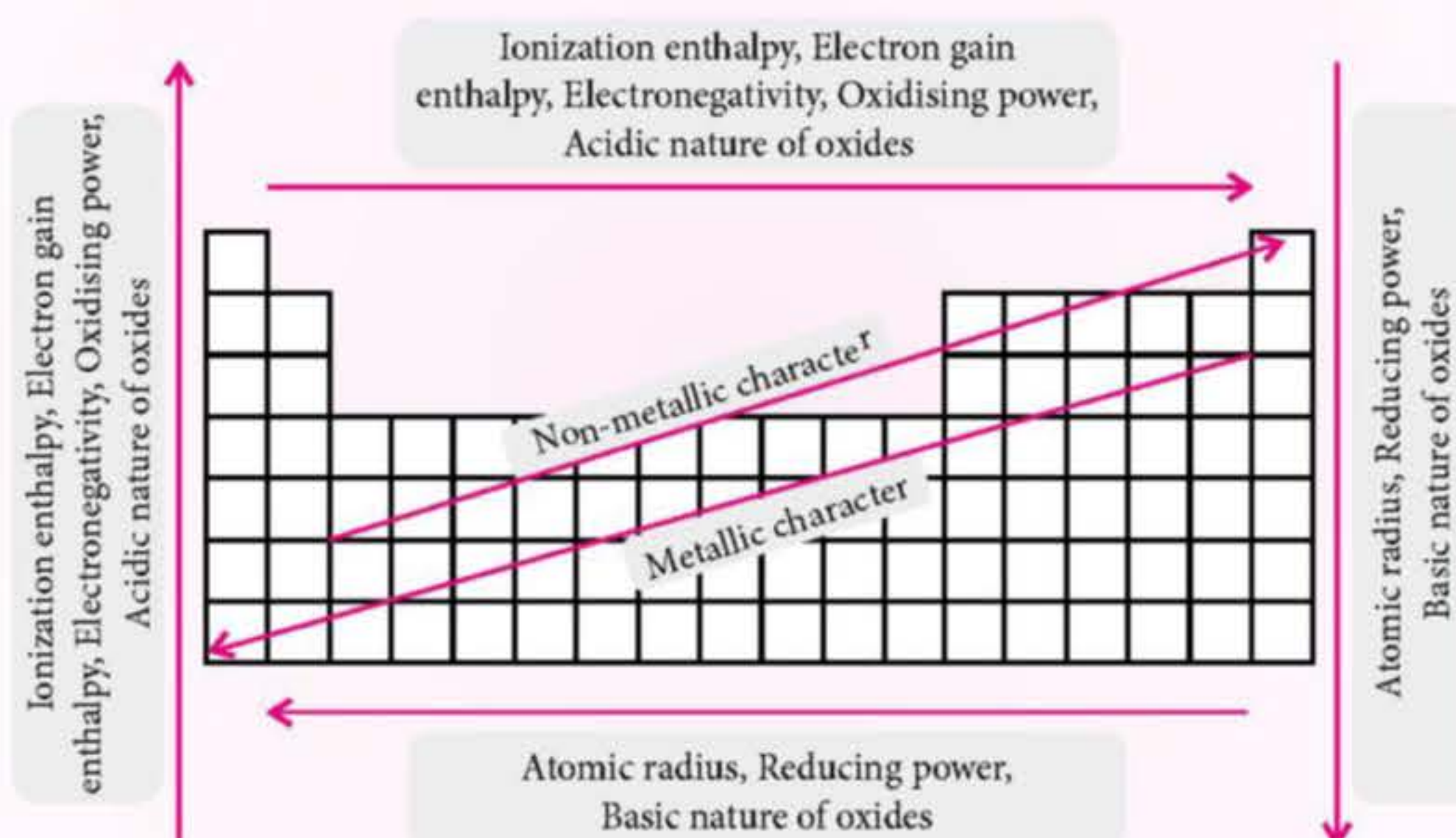
- For a reaction, $aA + bB \rightleftharpoons cC + dD$
 $\frac{k_f}{k_b} = K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$; $K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$; $K_p = K_c (RT)^{\Delta n}$
- $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$; $K = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2$
- $K_w = K_a \times K_b$; $K_{sp} = [A^{y+}]^x \cdot [B^{x-}]^y$
- $\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$ (for salts of strong acid and weak base)
- $\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$ (for salts of weak acid and weak base)
- $\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$ (for salts of weak acid and strong base)

Hydrocarbons

- Conformations of ethane**: Staggered > Skew or Gauche > Eclipsed
- Conformations of cyclohexane**: Chair > Twist-boat > Boat > Half-chair
- Stability order of different alkenes**:
 $R_2C = CR_2 > R_2C = CHR > R_2C = CH_2 >$
 $\begin{matrix} R & & H \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ H & & R \end{matrix} > \begin{matrix} R & & R \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ H & & H \end{matrix} > RCH = CH_2 > CH_2 = CH_2$
- Acidity**: Alkynes > alkenes > alkanes (as s -character \propto acidity).
- Alkynes undergo electrophilic and nucleophilic addition reactions.
- Aromatic compounds**: Cyclic, completely conjugated system of p -orbitals in ring, planar, $(4n + 2)\pi$ e's.
- Anti-aromatic compounds**: Cyclic, completely conjugated system of p -orbitals in ring, planar, $4n$ π -e's.
- Non-aromatic compounds**: Does not satisfy any one or more of the above conditions.

Inorganic Chemistry

Classification of Elements and Periodicity in Properties



Chemical Bonding

Type of hybridisation	No. of hybrid orbitals	Shape of molecule	Bond angle
sp	2	Linear	180°
sp^2	3	Trigonal planar	120°
sp^3	4	Tetrahedral	109.5°
dsp^2	4	Square planar	90°
dsp^3 or sp^3d	5	Trigonal bipyramidal	120° and 90°
d^2sp^3 or sp^3d^2	6	Octahedral	90°
d^3sp^3 or sp^3d^3	7	Pentagonal bipyramidal	72° and 90°

Organic Chemistry

Some Basic Principles and Techniques

- **Preference order of functional groups :** Carboxylic acids > sulphonic acids > anhydrides > esters > acid chlorides > acid amides > nitriles > isocyanides > aldehydes > ketones > alcohols > phenols > thiols > amines > alkenes > alkynes
- **Stability order :**
Carbocations : $3^\circ > 2^\circ > 1^\circ > CH_3$; **Carbanions :** $CH_3 > 1^\circ > 2^\circ > 3^\circ$
Free radicals : $3^\circ > 2^\circ > 1^\circ > CH_3$
- **-I effect :** $-NO_2 > -CN > -COOH > -F > -Cl > -Br > -I > -H$
- **+I effect :** $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > CH_3- > D- > H-$
- **+R effect :** $-OH, -OR, -SH, -SR, -NH_2, -NHR, -NR_2, -Cl, -Br, -I$
- **-R effect :** $>C=O, -CHO, -COOR, -CN, -NO_2$

The s- and p-Block Elements

- **Basic strength :**
 $LiOH < NaOH < KOH < RbOH < CsOH$
 $- Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
 $- B(OH)_3 < Al(OH)_3 < Ga(OH)_3 < In(OH)_3 < Tl(OH)_3$
- **Stability :**
 $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$
 $- BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
 $- BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4 < BaSO_4$
- **Solubility :** $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
 $- BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$
Almost insoluble
- **Stability of oxidation states :**
 $B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$; $B^+ < Al^+ < Ga^+ < In^+ < Tl^+$; $Ge^{4+} > Sn^{4+} > Pb^{4+}$; $Ge^{2+} < Sn^{2+} < Pb^{2+}$
- **Lewis acid character :**
 $BX_3 > AlX_3 > GaX_3 > InX_3$; $BF_3 < BCl_3 < BBr_3 < BI_3$
- **Catenation tendency :** $C \gg Si > Ge \approx Sn \gg Pb$
- **Acidic strength :** Acidic strength of their oxides decreases down the group.

Quantitative Estimation

- **Liebig's combustion method :**
 $\% \text{ of C} = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of compound taken}} \times 100$
 $\% \text{ of H} = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of compound taken}} \times 100$
- **Dumas' method :**
 $\% \text{ of N} = \frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ at STP}}{\text{Wt. of compound}} \times 100$
- **Kjeldah's method :**
 $\% \text{ of N} = \frac{1.4 \times M_{\text{acid}} \times V_{\text{acid}} \times \text{Basicity of acid}}{\text{Wt. of compound}}$
- **Carius method :**
 $\% \text{ of X} = \frac{\text{At. wt. of X}}{108 + \text{At. wt. of X}} \times \frac{\text{Wt. of AgX formed}}{\text{Wt. of compound}} \times 100$
 $\% \text{ of S} = \frac{32}{233} \times \frac{\text{Wt. of } BaSO_4 \text{ formed}}{\text{Wt. of compound}} \times 100$
- **Ignition method :**
 $\% \text{ of P} = \frac{62}{222} \times \frac{\text{Wt. of } Mg_2P_2O_7 \text{ formed}}{\text{Wt. of compound}} \times 100$
- **Iodine method :**
 $\% \text{ of O} = \frac{32}{88} \times \frac{\text{Wt. of } CO_2 \text{ formed}}{\text{Wt. of compound}} \times 100$

Physical Chemistry

The Solid State

- Density of unit cell : $d = \frac{Z \times M}{a^3 \times N_A} \text{ g cm}^{-3}$

- Total no. of atoms per unit cell :

sc	bcc	fcc
$8 \times \frac{1}{8} = 1$	$8 \times \frac{1}{8} + 1 \times 1 = 2$	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

- Relation between d , a and r

sc	$r = \frac{d}{2} = \frac{a}{2}$ since $d = a$
fcc	$r = \frac{d}{2} = \frac{a}{2\sqrt{2}}$ since $d = \frac{a}{\sqrt{2}}$
bcc	$r = \frac{d}{2} = \frac{\sqrt{3}a}{4}$ since $d = \frac{\sqrt{3}a}{2}$

Solutions

- Expression for concentration of a solution :

$$M = \frac{w_2 \times 1000}{M_2 \times V_{(\text{in mL})}}; N = \frac{w_2 \times 1000}{E_2 \times V_{(\text{in mL})}}; m = \frac{w_2 \times 1000}{M_2 \times w_1}$$

$$x_2 = \frac{n_2}{n_1 + n_2}, x_1 = \frac{n_1}{n_1 + n_2}; \text{ppm} = \frac{w_2}{M_{\text{soln.}}} \times 10^6$$

- Henry's law : $p = K_H \cdot x$

- For liquid solutions : $p_A = x_A \times p_A^\circ; p_B = x_B \times p_B^\circ;$

$$P_{\text{total}} = p_A + p_B; y_A = p_A / (p_A + p_B), y_B = 1 - y_A$$

- Modified colligative properties : $\Delta T_b = iK_b \times m$

$$\Delta T_f = iK_f \times m; \pi = i \frac{n}{V} RT; \frac{p^\circ - p_s}{p^\circ} = ix_2$$

$$\alpha_{(\text{disso.})} = \frac{i-1}{n-1}; \alpha_{(\text{asso.})} = (1-i) \frac{n}{n-1}; i = \frac{M_c}{M_o}$$

Electrochemistry

- $R = \frac{V}{I}; G = \frac{1}{R}; \rho = R \frac{a}{l}; \kappa = G \times \frac{l}{a}$

- $\Lambda_{eq} = \kappa \times V = \kappa \times 1000 / N; \Lambda_m = \kappa \times V = \kappa \times 1000 / M$

- $\Lambda_m^c = \Lambda_m^\infty - A\sqrt{c}; \Lambda_{eq}^\infty = \lambda_c^\infty + \lambda_a^\infty; \Lambda_m^\infty = x\lambda_c^\infty + y\lambda_a^\infty$

- $\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty}; \Delta G^\circ = -nFE_{\text{cell}}^\circ = -RT \ln K_c$

- $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}; E_{\text{cell}}^\circ = \frac{0.0591}{n} \log K_c$

Chemical Kinetics

- Expressions for different orders :

Rate law	Integrated rate law	Half-life period
Rate = $k[A]^0$ [Zero order]	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0 / 2k$
Rate = $k[A]^1$ [1 st order]	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 0.693/k$
Rate = $k[A]^2$ [2 nd order]	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k[A]_0$
Rate = $k[A]^n$ [n th order]	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}$	$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$

- Arrhenius equation :

$$k = Ae^{-E_a/RT}; \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

- Collision theory : $k = P Z e^{-E_a/RT}$

where, P = steric factor ; Z = collision frequency

Surface Chemistry

- Freundlich adsorption isotherm : $\frac{x}{m} = kP^{1/n}$

- Langmuir adsorption isotherm : $\frac{x}{m} = \frac{aP}{1+bP}$

- Hardy-Schulze rule : Coagulation power for

-vely charged sols : $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$

+vely charged sols : $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

General Principles and Processes of Isolation of Elements

- Thermodynamic principles of metallurgy : For a reaction to occur, ΔG should be -ve. A reaction with ΔG + ve can be made to occur if it is coupled with another reaction having a large -ve ΔG , so that the net ΔG of both the reactions is -ve. *Ellingham Diagram* : Plots of $\Delta_f G^\circ$ vs T for formation of oxides. These help in predicting the feasibility of thermal reduction of an ore.

- For most of the reactions of formation of $M_xO_{(s)}$, slope = +ve, because ΔG° increases with rise in T .

- Each curve is a straight line except when phase changes take place (solid \rightarrow liquid, liquid \rightarrow gas).

- Metal oxide placed higher in the diagram can be reduced by the metal placed lower.

Inorganic Chemistry

The p-Block Elements

- **Group 15 (Nitrogen family) :**
 - Bond angle, Thermal stability and Basic strength : $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
 - B.Pt. : $\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3 < \text{BiH}_3$
 - Reducing nature : $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3$
- **Group 16 (Oxygen family) :**
 - Bond angle and Thermal stability : $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$
 - Acidic character and Reducing nature : $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$
- **Group 17 (Halogen family) :**
 - Oxidizing power : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
 - B.Pt. and M.Pt. : $\text{HF} > \text{HCl} < \text{HBr} < \text{HI}$
 - Bond length, Acidic strength and Reducing nature : $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$
- **Group 18 (Noble gases) :**
 - M.Pt., B.Pt., Ease of liquefaction, Solubility, Adsorption and Polarizability : $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$
 - Thermal conductivity : $\text{He} > \text{Ne} > \text{Ar} > \text{Kr} > \text{Xe}$

d- and f-Block Elements

- **d-block elements :** $(n-1)d^{1-10} ns^{0-2}$
 - Atomic radii decreases with increase in atomic number.
 - Atomic radii of the pairs are almost same because of Lanthanide contraction. [Zr-Hf, Nb-Ta, Mo-W, Ag-Au]
 - They show variable oxidation states.
 - They form complexes, interstitial compounds and alloys.
 - They also act as catalyst.
- **f-block elements :** $(n-2)f^{1-14}(n-1)d^{0-1} ns^2$
 - $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$: Basicity decreases
 - La^{3+} to Lu^{3+} : Tendency to form complexes increases

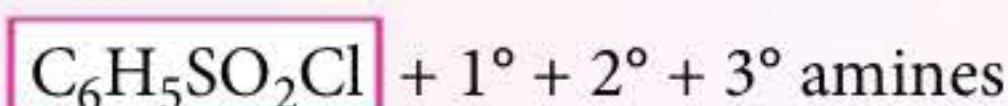
Coordination Compounds

- **Spectrochemical series :**
 $\text{I}^- < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^- < \text{CO}$
- Magnetic moment, $\mu = \sqrt{n(n+2)}$ B.M.; $\Delta_t = 4/9\Delta_o$
- CFSE = $(-0.4x + 0.6y)\Delta_o$ where, x = no. of e^- s in t_{2g} orbitals, y = no. of e^- s in e_g orbitals.

Amines

- **Basic nature :** Aliphatic amine $>$ NH_3 $>$ aromatic amine
 - $3^\circ > 2^\circ > 1^\circ > \text{NH}_3$ [in gas phase/in non-aq. solvent]
 - $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$ [in aq. phase, only $-\text{CH}_3$ subs. amines]
 - $2^\circ > 3^\circ > 1^\circ > \text{NH}_3$ [in aq. phase, for $-\text{C}_2\text{H}_5$ or higher subs. amines]

- **Hinsberg's test :**



- Clear solution $\xrightarrow{\text{KOH}}$ Soluble salt [For 1° amine]
- Ppt. $\xrightarrow{\text{KOH}}$ Insoluble [For 2° amine]
- No reaction [For 3° amine]

Organic Chemistry

Haloalkanes and Haloarenes

- **Reactivity order :** $\text{RI} > \text{RBr} > \text{RCl}$
 - $\text{S}_{\text{N}}1$ reaction : $3^\circ > 2^\circ > 1^\circ$
 - $\text{S}_{\text{N}}2$ reaction : $1^\circ > 2^\circ > 3^\circ$
- **Elimination reaction :**
 - $\text{E}1$: Reactivity of alkyl halides : $3^\circ > 2^\circ > 1^\circ$.
 - $\text{E}2$: Favourable $\rightarrow 1^\circ$ alkyl halide in presence of strong base.

Alcohols, Phenols and Ethers

- **Acidity :** Phenols $>$ water $>$ 1° alcohol $>$ 2° alcohol $>$ 3° alcohol
- **Distinction test of alcohols :**

Alcohol	Dichromate (Oxidation) test	Victor Meyer's test	Lucas test
1°	Acid (Orange solution becomes green)	Blood red colour	No turbidity
2°	Ketone (Orange solution becomes green)	Blue colour	Turbidity in 5 minutes
3°	No reaction	Colourless	Turbidity immediately

- **Distinction test of phenol :**

Test	Observation
FeCl_3 test	Violet colour
$\text{Br}_2 - \text{H}_2\text{O}$ test	White ppt.
Liebermann's nitroso test ($\text{NaNO}_2 + \text{conc. H}_2\text{SO}_4$)	Deep green/blue colour which changes into red on dilution.

Aldehydes, Ketones and Carboxylic Acids

- **Reactivity order towards S_{N} reactions :** $\text{HCHO} > \text{RCHO} > \text{PhCHO} > \text{RCOR} > \text{RCOPh} > \text{PhCOPh}$
- **Distinction test of aldehydes & ketones :**

Test	Aldehydes	Ketones
Fehling's solution	Red ppt.	No ppt.
Tollens' reagent	Silver mirror	No ppt.

- **Distinction test of carboxylic acids :**

Test	Carboxylic acids	Phenols
NaHCO_3	Brisk effervescence of CO_2 gas	No reaction
FeCl_3	Buff coloured ppt.	Violet colour

Biomolecules

- **Reducing sugars :** All monosaccharides
- **Non reducing sugars :** All polysaccharides and disaccharides like sucrose.
- **Isoelectric point :** pH at which no net migration of amino acid under electric field.