

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  $r$ :
 
$$sc: r = \frac{a}{2}, fcc: r = \frac{a}{2\sqrt{2}}, bcc: r = \frac{a\sqrt{3}}{4}$$
- Coordination number and packing efficiency:
  - sc: CN = 6, PE = 52.4%; bcc: CN = 8, PE = 68%;
  - fcc: CN = 12, PE = 74%
- Size and no. of voids:
 

| Type        | Size    | No. of Voids |
|-------------|---------|--------------|
| Octahedral  | 0.414 R | N            |
| Tetrahedral | 0.225 R | 2N           |

Solutions

- Expression for concentration of a solution:
 
$$M = \frac{w_2 \times 1000}{M_2 \times V(\text{in l})}, N = \frac{w_2 \times 1000}{E_2 \times V(\text{in ml})}$$

$$x_2 = \frac{n_2}{n_1 + n_2}, x_1 = \frac{n_1}{n_1 + n_2}; \text{ppm} = \frac{w_2}{M_{\text{soln}}} \times 10^6$$
- On mixing solutions:  $N_1 V_1 + N_2 V_2 = N_3 (V_1 + V_2)$   
 $M_1 V_1 + M_2 V_2 = M_3 (V_1 + V_2)$
- For liquid solutions:  $p_A = x_A \cdot p_A^\circ; p_B = x_B \cdot p_B^\circ$   
 $P_{\text{total}} = p_A + p_B; \frac{P_A}{P_{\text{total}}} = \frac{p_A^\circ}{p_A^\circ + p_B^\circ} \cdot \frac{x_A}{x_A + x_B} = \frac{P_A^\circ}{P_{\text{total}}^\circ} \cdot x_A$
- Colligative properties:  $\Delta T_f = i K_f \times m; \Delta T_b = i K_b \times m$   
 $\Delta T_f = i K_f \times m; \pi = \left(\frac{n}{V}\right) \frac{RT}{M}; \frac{P_2}{P_1} = \frac{M_2}{M_1}$   
 $\alpha_{\text{disso.}} = \frac{i-1}{n-1}; \alpha_{\text{assoc.}} = \left(1 - \frac{n}{i}\right)$   
 $i = \frac{M_c}{M_n} \text{ or } \frac{C_c}{C_n} \text{ (where } M = \text{molar mass, } C = \text{colligative property)}$

Electrochemistry

- $R = \frac{V}{I}; G = \frac{1}{R}; \rho = R \frac{l}{A}; K = G \times \frac{l}{A}$
- $\Lambda_{\text{eq}} = k \times V = k \times \frac{1000}{N}; \Lambda_m = k \times V = k \times \frac{1000}{M}$
- $\Lambda_m^\infty = \Lambda_m^\infty - b\sqrt{C}; \Lambda_m^\infty = \lambda_{\text{c}}^\infty + \lambda_{\text{a}}^\infty; \Lambda_m^\infty = x\lambda_{\text{c}}^\infty + y\lambda_{\text{a}}^\infty$
- $\Delta G = -nFE_{\text{cell}} = -RT \ln K$
- $W = ZIt; \frac{W_1}{W_2} = \frac{E_1}{E_2}; E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}; E_{\text{in vacuo}}$
- $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{1}{[\text{A}^{2+}]}; E_{\text{cell}}^\circ = \frac{0.059}{n} \log K_c$

Chemical Kinetics

- Expressions for different orders:
 

| Rate law                                | Integrated rate law                                     | Half-life                          |
|---|---|------------------------------------|
| Rate = $k[A]^2$ (bimol)                 | $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$                  | $t_{1/2} = \frac{1}{k[A]_0}$       |
| Rate = $k[A]^2$ (1 <sup>st</sup> order) | $\ln[A]_0 - \ln[A] = kt$                                | $t_{1/2} = \frac{0.693}{k}$        |
| Rate = $k[A]^2$ (1 <sup>st</sup> order) | $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$                  | $t_{1/2} = \frac{1}{k[A]_0}$       |
| Rate = $k[A]$ (1 <sup>st</sup> order)   | $\ln[A]_0 - \ln[A] = kt$                                | $t_{1/2} = \frac{0.693}{k}$        |
| Rate = $k[A]^n$ (n <sup>th</sup> order) | $\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt$ | $t_{1/2} = \frac{1}{k[A]_0^{n-1}}$ |
- Arrhenius equation:
 
$$k = A e^{-\frac{E_a}{RT}}; \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Surface Chemistry

- vely charged sols: Metals, sulphides, acidic dyes, starch, clay, silk.
- vely charged sols: Metal hydroxides, oxides, basic dyes, haemoglobin.
- Hardy-Schulze rule: Coagulation power for -vely charged sols:  $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$
- vely charged sols:  $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

Inorganic Chemistry

General Principles and Processes of Isolation of Elements

- Main steps involved in extraction of metals:
  - Concentration of the ore: Hydraulic separation: for oxide ores; Froth floatation: for sulphide ores; Electromagnetic separation: for magnetic impurities; Leaching: chemical method.
  - Conversion of ore to oxide: Calcination: for carbonates and hydrated oxides; Roasting: for sulphide ores.
  - Reduction of oxide into free metal: Smelting: Reduction with carbon; Aluminothermic process: Reduction with Al; Auto-reduction: for less electropositive metals; Electrorefining: Electrolysis of fused oxide.
  - Refining of crude metal: Liquation: for metals having low mp; Distillation: for volatile metals; Poling: for metals having own oxides as impurities; Electrorefining: for Cu, Ag, Au, Ni, Cr, Al; Zone refining: for Si, Ge, Ga; van Arkel method: for Ti, Zr; Chromatography: for elements available in minute quantities.

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.P. and M.P.:  $\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3 < \text{BiH}_3$
  - M.P.:  $\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$
  - Reducing nature:  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3$
  - Bond angle:  $\text{PF}_3 < \text{PCl}_3 < \text{PR}_3 < \text{PI}_3$
  - Lewis acid strength:  $\text{PCl}_3 > \text{AsCl}_3 > \text{SbCl}_3 > \text{BiCl}_3 > \text{PBr}_3 > \text{PBr}_5 > \text{PI}_3$
- Group 16 (Oxygen family): Bond angle and Thermal stability:  $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$ 
  - Volatility:  $\text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te} > \text{H}_2\text{O}$
  - Acidic strength and Reducing nature:  $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$
  - Stability:  $\text{SF}_6 > \text{SeF}_6 > \text{TeF}_6$
- Group 17 (Halogen family):
  - Oxidizing power:  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
  - B.P. and M.P.:  $\text{HI} > \text{HCl} < \text{HBr} < \text{HI}$
  - Dipole moment and Thermal stability:  $\text{HI} > \text{HCl} > \text{HBr} > \text{HI}$
  - Bond length, Acidity strength and Reducing nature:  $\text{HI} < \text{HCl} < \text{HBr} < \text{HI}$
  - Acidic strength:  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$ ;  $\text{HBrO} < \text{HBrO}_2 < \text{HBrO}_3 < \text{HBrO}_4$ ;  $\text{HIO} < \text{HIO}_2 < \text{HIO}_3 < \text{HIO}_4$
  - Oxidizing power:  $\text{HClO} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$
- Group 18 (Noble gases): M.P., B.P., 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:  $(n-1)d^1-10(n-1)s^2$ 
  - 3d series:  $3d^1-3d^{10}$
  - 4d series:  $4d^1-4d^{10}$ ; 5d series:  $5d^1-5d^{10}$
  - Acidic character:  $\text{MnO} < \text{Mn}_2\text{O}_3 < \text{MnO}_2 < \text{Mn}_2\text{O}_7$ ; Ionic character:  $\text{MnO} > \text{Mn}_2\text{O}_3 > \text{Mn}_2\text{O}_7 > \text{MnO}_2$
- f-block elements:  $(n-2)f^1-14(n-1)d^0(n-1)s^2$ 
  - $\text{La}(\text{OH})_3$  to  $\text{Lu}(\text{OH})_3$ ; Basicity decreases;  $\text{La}^{3+}$  to  $\text{Lu}^{3+}$ ; Tendency to form complexes increases.

Coordination Compounds

- Coordination number:
 

|                     |                       |                     |
|---------------------|-----------------------|---------------------|
| Coordination number | Coordination geometry | Coordination number |
| 2                   | Linear                | 6                   |
| 4                   | Tetrahedral           | 6                   |
| 4                   | Square planar         | 6                   |
| 6                   | Octahedral            | 6                   |
- Spectrochemical series:
 
$$\text{I}^- < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{N}_3^- < \text{ox}^{2-} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^- < \text{CO}$$
- $\mu = \sqrt{n(n+2)} \text{ B.M.}; \Delta_o = \frac{4}{9} \Delta_t$
- CFSE =  $(-0.4x + 0.6y)\Delta_o$  where  $x = \text{no. of } e \text{ in } t_{2g} \text{ orbitals, } y = \text{no. of } e \text{ in } e_g \text{ orbitals}$

Organic Chemistry

Haloalkanes and Haloarenes

- Reactivity order:  $\text{RI} > \text{RBr} > \text{RCl} > \text{R}^3\text{I} > \text{R}^2\text{I} > \text{RI} > \text{R}^3\text{Cl} > \text{R}^2\text{Cl} > \text{RCl} > \text{R}^3\text{Br} > \text{R}^2\text{Br} > \text{RBr} > \text{R}^3\text{I} > \text{R}^2\text{I} > \text{RI}$
- Dipole moments:
  - $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$
  - $\text{CH}_2\text{Cl}_2 > \text{CH}_2\text{Cl}_2 > \text{CH}_2\text{Cl}_2 > \text{CCl}_4(\text{zero})$
  - $o\text{-Dichlorobenzene} > m\text{-dichlorobenzene} = \text{chlorobenzene} > p\text{-dichlorobenzene}(\text{zero})$

Alcohols, Phenols and Ethers

- Acidity: Phenols  $>$  water  $>$  1<sup>st</sup> alcohol  $>$  2<sup>nd</sup> alcohol  $>$  3<sup>rd</sup> alcohol
- Distinction test of alcohols:
 

| Alcohol         | Dichromate (Oxidation) test            | Victor Meyer's test | Lucas test               |
|-----------------|--|---------------------|--------------------------|
| 1 <sup>st</sup> | Acid (Orange solution becomes green)   | Colourless          | No turbidity             |
| 2 <sup>nd</sup> | Ketone (Orange solution becomes green) | Blue colour         | Turbidity (5-10 minutes) |
| 3 <sup>rd</sup> | No reaction                            | Colourless          | Turbidity immediately    |

Distinction test of phenol:

| Test   | Observation  |
|--|--|
| FeCl <sub>3</sub> test   | Violet colour  |
| Br <sub>2</sub> -H <sub>2</sub> O test   | White ppt.   |
| Libermann's nitroso test (NaNO <sub>2</sub> + conc. H <sub>2</sub> SO <sub>4</sub> ) | Deep green/blue colour which changes into red on dilution. |
| Azo dye test   | Orange colour  |

Aldehydes, Ketones and Carboxylic Acids

- Reactivity order towards  $\text{S}_\text{N}2$  reactions:  $\text{ClCHO} > \text{RCHO} > \text{PhCHO} > \text{RCOR} > \text{RCOPh} > \text{PhCOPh}$
- Distinction test of aldehydes & ketones:
 

| Test               | Aldehydes     | Ketones   |
|--------------------|---------------|-----------|
| Schiff's reagent   | Pink colour   | No colour |
| Fehling's solution | Red ppt.      | No ppt.   |
| Tollens' reagent   | Silver mirror | No ppt.   |
- Acidity: Carboxylic acids  $>$  Phenols  $>$  Alcohols
- Distinction test of carboxylic acids:
 

| Test             | Carboxylic acids                        | Phenols       |
|------------------|---|---------------|
| $\text{NaHCO}_3$ | Risk effervescence of $\text{CO}_2$ gas | No reaction   |
| $\text{FeCl}_3$  | Buff coloured ppt.                      | Violet colour |

Amines

- Basic nature: Aliphatic amine  $>$   $\text{NH}_3$   $>$  aromatic amine;  $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$  (in gas phase in non-aq. soln);  $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$  (in aq. phase only - CH<sub>3</sub> groups raises);  $2^\circ > 3^\circ > 1^\circ > \text{NH}_3$  (in aq. phase only - CH<sub>3</sub> groups raises)
- Distinction test (Hinsberg's test):
 
$$\text{C}_6\text{H}_5\text{N}_2\text{SO}_2\text{Cl} + 1^\circ, 2^\circ \text{ or } 3^\circ \text{ amines}$$
  - Clear solution  $\xrightarrow{\text{KOH}}$  soluble salt (1<sup>st</sup> amine)
  - ppt  $\xrightarrow{\text{KOH}}$  No reaction (1<sup>st</sup> amine)
  - No reaction (3<sup>rd</sup> amine)
  - $\text{ArN}^+\text{X}^-$  are more stable than  $\text{RN}^+\text{X}^-$
  - EDGs stabilise while EWGs destabilise the diazonium salts.

Biomolecules

- Reducing sugars: All monosaccharides
- Non-reducing sugars: All polysaccharides and disaccharides like sucrose.
- Fat soluble vitamins: A, D, E and K.
- Water soluble vitamins: B<sub>1</sub>, B<sub>2</sub>, B<sub>6</sub>, B<sub>12</sub> and C.

Polymers

- Addition homopolymers: Polythene, polystyrene
- Condensation homopolymers: Nylon-6, PHE
- Addition copolymers: Buna-S, Buna-N
- Condensation copolymers: Nylon-6, PHE
- Biodegradable copolymers: PHBV, Nylon-2, myosin