

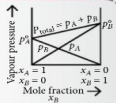
# CONCEPT MAP

## SURE SHOT TOPICS OF PHYSICAL CHEMISTRY (SOLUTIONS, ELECTROCHEMISTRY, CHEMICAL KINETICS AND SURFACE CHEMISTRY)

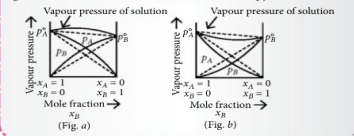
### Solutions

- Henry's law:**  $p = K_H x$  (where,  $K_H$  is Henry's law constant.)
- Raoult's law:** For a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.  $p_1 = p_1^* x_1$  and  $p_2 = p_2^* x_2$ ; where,  $p_1^*$  and  $p_2^*$  are vapour pressures of pure components 1 and 2 respectively, at the same temperature.
- Dalton's law of partial pressure:**  $p_{total} = p_1 + p_2 = x_1 p_1^* + x_2 p_2^* = (1 - x_2) p_1^* + x_2 p_2^* = p_1^* + (p_2^* - p_1^*) x_2$

- Ideal Solutions:**  $A - B$  interactions =  $A - A$  and  $B - B$  interactions  
 $\Delta H_{mix} = 0, \Delta V_{mix} = 0$   
e.g., dilute solutions, benzene + toluene,  $n$ -hexane +  $n$ -heptane.



- Positive deviation from Raoult's law:**  $A - B$  interactions <  $A - A$  and  $B - B$  interactions;  $\Delta H_{mix} > 0, \Delta V_{mix} > 0$  (Fig. a).  
e.g., acetone + ethanol, acetone +  $CS_2$ , water + methanol.
- Negative deviation from Raoult's law:**  $A - B$  interactions >  $A - A$  and  $B - B$  interactions;  $\Delta H_{mix} < 0, \Delta V_{mix} < 0$  (Fig. b).  
e.g., acetone + aniline, HCl + water, acetic acid + pyridine.



### Colligative Properties

- Relative Lowering of Vapour Pressure:**  
 $\frac{p_1 - p_1^*}{p_1^*} = x_2 = \frac{n_2}{n_1 + n_2} = \frac{w_2 \times M_1}{M_1 \times w_1 + w_2 \times M_2}$  (for dilute solutions,  $n_2 \ll n_1$ )

- Elevation in boiling point:**  $\Delta T_b = T_b - T_b^*$   
 $\Delta T_b \propto m$  or  $\Delta T_b = K_b m = K_b \left( \frac{w_2 \times 1000}{M_2 \times w_1 (\text{in g})} \right)$

- Depression in freezing point:**  $\Delta T_f = T_f^* - T_f$   
 $\Delta T_f \propto m$  or  $\Delta T_f = K_f m = K_f \left( \frac{w_2 \times 1000}{M_2 \times w_1 (\text{in g})} \right)$

- Osmotic pressure:**  $\pi = CRT = \left( \frac{w_2}{V} \right) \frac{RT}{M_2}$   
 $\pi V = w_2 RT / M_2$  or  $M_2 = w_2 RT / \pi V$

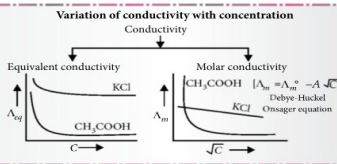
- van't Hoff Factor:** It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.
- If  $i > 1$ , solute undergoes dissociation in the solution and if  $i < 1$ , solute undergoes association in the solution.  
 $\alpha_{dissociation} = i - 1 / n - 1$ ;  $\alpha_{association} = (1 - i) / n - 1$

### Electrochemistry

Type	Energy change	Anode	Cathode
Electrolytic cell	Electrical energy $\rightarrow$ Chemical energy	+	-
Galvanic (voltaic) cell	Chemical energy $\rightarrow$ Electrical energy	-	+

- EMF of cell:**  $E_{cell}^{\circ} = E_{right}^{\circ} - E_{left}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$
- Nernst equation:** For a reaction,  $M^{n+}(aq) + ne^{-} \rightarrow M(s)$   
 $E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$ ;  $E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}(aq)]}$
- Relation between cell potential and Gibbs energy change:**  
 $\Delta G^{\circ} = -nFE_{cell}^{\circ}$ ;  $\Delta G^{\circ} = -2.303 RT \log K_c$

Specific Conductance	Equivalent Conductance	Molar Conductance
Formula $\kappa = \frac{l}{a}$	$\Lambda_{eq} = \kappa \times \frac{1000}{\text{Normality}}$	$\Lambda_m = \kappa \times \frac{1000}{\text{Molarity}}$



- Kohlrausch's law:** For an electrolyte,  $A_x B_y$   
 $\Lambda_m^{\circ} = x\lambda_1^{\circ} + y\lambda_2^{\circ}$  or  $\Lambda_{eq}^{\circ} = \lambda_1^{\circ} + \lambda_2^{\circ}$
- Degree of dissociation ( $\alpha$ ):**  $\alpha = \Lambda_m / \Lambda_m^{\circ}$
- Faraday's first law of electrolysis:**  $w \propto Q$   
 $w = ZQ = Z \times I \times t$ ;  $Z = \frac{Eq. wt. of substance}{96500}$
- Faraday's second law of electrolysis:**  $w_1 / w_2 = E_1 / E_2$

Cell	Anode Reaction	Cathode Reaction
Dry cell	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$	$MnO_2(s) + NH_4^+(aq) + e^{-} \rightarrow Mn(OH)(s) + NH_3(g)$
Mercury cell	$Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^{-}$	$HgO(s) + H_2O(l) + 2e^{-} \rightarrow Hg(l) + 2OH^-(aq)$
Lead storage cell	$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^{-}$	$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^{-} \rightarrow PbSO_4(s) + 2H_2O(l)$
Nickel-Cadmium cell	$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^{-}$	$NiO_2(s) + 2H_2O(l) + 2e^{-} \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$
Fuel cell	$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^{-}$	$2O_2(g) + 2H_2O(l) + 4e^{-} \rightarrow 4OH^-(aq)$

### Chemical Kinetics

Rate law, integrated rate law, half-life, units of rate constant and graph for the reactions of different orders:

Order	Rate law	Integrated rate law
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$
1	Rate = $k[A]^1$	$\ln[A]_t = -kt + \ln[A]_0$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$
2	Rate = $k[A][B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]_t}{[A]_0[B]_t}$
n	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]_0^{n-1}} - \frac{1}{[A]_t^{n-1}}$

Order	Half-life	Units of rate constant	Graph
0	$t_{1/2} = [A]_0 / 2k$	$\text{mol L}^{-1} \text{s}^{-1}$	$[A]$ vs $t$ ; slope = $-k$
1	$t_{1/2} = 0.693/k$	$\text{s}^{-1}$	$\ln[A]$ vs $t$ ; slope = $-k$
1	$t_{1/2} = 1/k[A]_0$	$\text{L mol}^{-1} \text{s}^{-1}$	$1/[A]$ vs $t$ ; slope = $k$
2	-	$\text{L mol}^{-1} \text{s}^{-1}$	$1/[A]$ vs $t$ ; slope = $k$
n	$t_{1/2} = \frac{2^{1/n} - 1}{k_n(n-1)[A]_0^{n-1}}$	$(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$	$\frac{1}{[A]^{n-1}}$ vs $t$ ; slope = $k$

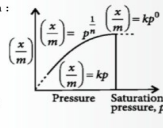
- Relationships between time periods for different fractions of reaction of first order to complete:**  
 $t_{3/4}$  or  $t_{75\%} = 2t_{1/2}$ ;  $t_{87.5\%} = 3t_{1/2}$ ;  $t_{93.75\%} = 4t_{1/2}$ ,  
 $t_{96.87\%} = 5t_{1/2}$ ;  $t_{99.9\%} = 10t_{1/2}$

- Arrhenius equation:**  $k = Ae^{-E_a/RT}$   
 $\log k = \log A - \frac{E_a}{2.303 RT}$ ;  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$
- Collision theory:**  $k = PZ \cdot e^{-E_a/RT}$  where,  $P$  = orientation factor or probability factor,  $Z$  = collision frequency.
- Rate of radioactive disintegration/Decay:** It follows first order kinetics.  
Disintegration constant ( $k$ ) =  $\frac{2.303}{t} \log \frac{N_0}{N}$  or  $\frac{2.303}{t} \log \frac{a}{a-x}$  ( $N_0$  = initial no. of atoms,  $N$  = atoms present at time  $t$ ,  $a$  = initial amount,  $x$  = amount disintegrated in time  $t$ ).  
Half-life ( $t_{1/2}$ ) =  $0.693/k$  and average life ( $\tau$ ) =  $1/k = t_{1/2} / 0.693$ .

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### Surface Chemistry

- Adsorption:** The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid.
- Physisorption:** Molecules are held by weak van der Waals' forces. Low heat of adsorption and non-specific. Decreases with increase in temperature. Forms multimolecular layer and is reversible.
- Chemisorption:** Molecules are held by strong chemical bonds. High heat of adsorption and specific. Increases with increase in temperature. Forms unimolecular layer and is irreversible.
- Positive adsorption:** Concentration of the adsorbate is more on the surface of the adsorbent than in the bulk.
- Negative adsorption:** Concentration of the adsorbate increases in the bulk after adsorption.
- Freundlich adsorption isotherm:**  
For low pressure,  $x/m \propto p$   
For high pressure,  $x/m \propto p^n$   
For intermediate pressures,  $x/m \propto p^{1/n}$  ( $n > 1$ )  
 $\log \frac{x}{m} = \log k + \frac{1}{n} \log p$
- Langmuir adsorption isotherm:**  
 $\frac{x}{m} = \frac{Kp}{1 + Kp}$



- Catalysis:** The phenomenon of enhancing the rate of a chemical reaction by using a catalyst.
- Selectivity:** Ability of a catalyst to direct the reaction to yield a particular product.
- Activity:** Capacity to increase the speed of the chemical reaction.

- Colloids:** A heterogeneous system in which particle size is between 1 and 1000 nm.
- Based on physical state of dispersed phase and dispersion medium:**
  - Sols:** Solids in liquids e.g., paints
  - Gels:** Liquids in solids e.g., cheese
  - Emulsions:** Liquids in liquids.
    - Oil in water type emulsions e.g., milk.
    - Water in oil type emulsions e.g., butter.
- Based on nature of interaction between dispersed phase and dispersion medium:**
  - Lyophilic colloids:** Liquid-loving, directly formed, reversible in nature, quite stable, cannot be easily coagulated.
  - Lyophobic colloids:** Liquid-hating, prepared by special methods, readily coagulated, irreversible, not stable, and need stabilising agents for their preservation.
- Based on type of particles of the dispersed phase:**
  - Multimolecular colloids:** Formed by aggregation of a large number of atoms or molecules (diameter < 1 nm) held by weak van der Waals' forces.
  - Macromolecular colloids:** Formed by molecules of large size.
  - Associated colloids:** Formed by substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates (called micelles).