

CONCEPT MAP

PHYSICAL CHEMISTRY (Part-I)

Solutions, Electrochemistry and Chemical Kinetics form the basis of physical chemistry and give an idea about the nature of solutions, relationship between chemical energy and electrical energy in redox reactions and also the rates of reactions.

SOLUTIONS

Expressing Concentration of Solutions

- **Mass percentage:** Grams of solute in 100 g of solution.
- **Strength:** Grams of solute in 1 L of solution.
- **Molarity:** Moles of solute in 1 L of solution.
- **Normality:** Gram equivalents of solute in 1 L of solution.
- **Molality:** Moles of solute in 1 kg of solvent.
- **Mole fraction:** Moles of the component / total no. of moles of all components.
- **Parts per million:** Mass of solute in one million (10<sup>6</sup>) parts by mass of solution.

Laws

- **Henry's law:**  $p = K \cdot p$  or  $p = K_H \cdot x$  where  $K_H$  is Henry's constant having units of pressure.
- **Raoult's law:**  
For non-volatile solute:  $\frac{p^0 - p_s}{p^0} = \frac{n_2}{n_1 + n_2} = x_2$   
For volatile components:  
 $p_A = x_A p_A^0$ ;  $p_B = x_B p_B^0$  and  $p_{total} = p_A + p_B$

Types of Solutions

- **Ideal solutions:** A-B interactions are of same magnitude as A-A and B-B interactions,  $\Delta V_{mix} = 0$  and  $\Delta H_{mix} = 0$ .
- **Non ideal solutions:** A-B interactions are of different magnitude than A-A and B-B interactions,  $\Delta V_{mix} \neq 0$  and  $\Delta H_{mix} \neq 0$ .  
Non ideal solutions showing +ve deviations: A-B interactions are weaker than A-A and B-B interactions,  $\Delta V_{mix} = +ve$ ,  $\Delta H_{mix} = +ve$  and resulting vapour pressure is higher than that expected.  
Non-ideal solutions showing -ve deviations: A-B interactions are stronger than A-A and B-B interactions,  $\Delta V_{mix} = -ve$ ,  $\Delta H_{mix} = -ve$  and resulting vapour pressure is lower than that expected.
- **Azotropes:** Constant boiling mixtures.

Colligative Properties

- Colligative properties depend only on the number of particles of solute dissolved in a definite amount of solvent. These are:  
- **Elevation in boiling point:** Boiling point of solution is higher than that of pure solvent.  $\Delta T_b = T_b - T_b^0 = K_b \cdot m$   
- **Depression in freezing point:** Freezing point of solution is lower than that of pure solvent.  $\Delta T_f = T_f^0 - T_f = K_f \cdot m$   
- **Relative lowering of vapour pressure:**  
 $\frac{p^0 - p_s}{p^0} = x_2 = \frac{n_2}{n_1}$  (for dilute solutions;  $n_1 \ll n_2$ )  
 $\frac{p^0 - p_s}{p_s} = \frac{n_2}{n_1}$  (for dilute as well as concentrated solutions)  
Osmotic pressure  $\pi = CRT$

van't Hoff Factor (i) and its Significance

- $i = \frac{\text{Observed value of colligative property}}{\text{Normal value of colligative property}} = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$
- For solute undergoing association:  
 $i = \frac{\alpha}{1 - \alpha} = \frac{1 - \alpha}{1 - \alpha} = 1 - \alpha < 1$   
(Degree of association)
- For solute undergoing dissociation:  
 $i = \frac{\alpha}{1 - \alpha} = \frac{1 - \alpha}{1 - \alpha} = 1 + \alpha > 1$   
(Degree of dissociation)
- **Modified colligative properties:**  
 $\frac{p^0 - p_s}{p^0} = i x_2$ ;  $\Delta T_b = i K_b m$ ;  $\Delta T_f = i K_f m$   
 $\pi = i CRT$

ELECTROCHEMISTRY

Basic Terms

- **Conductance:** Reciprocal of resistance.  
 $G = \frac{1}{R}$ ; Unit:  $\Omega^{-1}$  or S
- **Conductivity:** Conductance of 1 cm<sup>2</sup> of the conductor.  
 $\kappa = G \times \frac{l}{a}$ ; Unit:  $\Omega^{-1} \text{ cm}^{-1}$  or  $\text{S cm}^{-1}$
- **Equivalent conductivity:** Conductance of a solution containing 1 g-equivalent of an electrolyte dissolved in V cm<sup>3</sup> of the solution.  
 $\Lambda_{eq} = \frac{\kappa \times 1000}{\text{Normality}}$ ; Unit:  $\text{S cm}^2 \text{ eq}^{-1}$
- **Molar conductivity:** Conductance of a solution containing 1 mole of an electrolyte dissolved in V cm<sup>3</sup> of the solution.  
 $\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$ ; Unit:  $\text{S cm}^2 \text{ mol}^{-1}$
- **Electrode potential:** Tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions.
- **Cell potential or EMF of the cell:** The difference between electrode potentials of two half-cells.

Types of Cells

- **Electrochemical cell:** Device used to convert chemical energy of a redox reaction into electrical energy.
- **Electrolytic cell:** Device which uses electricity to bring about a non spontaneous redox reaction.

Laws

- **Faraday's first law:**  $W = ZIt$
- **Faraday's second law:**  $\frac{W_1}{W_2} = \frac{E_1}{E_2}$
- **Kohlrausch's law:** For an electrolyte  $A_x B_y$ ,  $\Lambda_m^0 = x \lambda_A^0 + y \lambda_B^0$  or  $\Lambda_m^0 = \lambda_A^0 + \lambda_B^0$

Nernst Equation and Electrochemical Series

- **Nernst equation:** For the reaction:  
 $M^{n+} + ne \rightarrow M$   
 $E = E^0 - \frac{57}{nF} \ln \frac{W}{[M^{n+}]}$  or  
 $E = E^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$  at 298 K
- **For concentration cell:**  
 $E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$ ;  $E_{cell} = +ve$  if  $C_2 > C_1$
- **For a reaction in equilibrium:**  
 $E_{cell}^0 = \frac{0.0591}{n} \log K$  at 298 K
- **Electrochemical series:** It is the arrangement of electrodes in order of increasing standard reduction potentials.  
- This series helps in comparing the relative oxidizing or reducing powers, relative activities of metals and to predict spontaneity of the redox reaction.

Commercial Cells/Batteries

- **Primary cells** cannot be recharged e.g., dry cell, mercury cell.
- **Secondary cells** can be recharged e.g., lead storage battery, Ni-Cd storage cell.
- **Fuel cells** convert the energy produced during combustion of fuels into electrical energy (e.g.,  $H_2-O_2$  fuel cell).

CHEMICAL KINETICS

Rate of Reaction

- For a reaction,  $aA + bB \rightarrow xX + yY$   
 $\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{x} \frac{d[X]}{dt} = \frac{1}{y} \frac{d[Y]}{dt}$
- Greater the concentration of reactants, faster is the reaction.
- Rate becomes double for every 10° rise in temperature.
- Greater the surface area of reactants, faster is the reaction.

Order and Molecularity

- For a rate law equation,  $\text{rate} = k[A]^m[B]^n$   
Order of reaction =  $m + n$ .
- **Molecularity** is the number of atoms, ions or molecules that must collide simultaneously with one another to result into a chemical reaction.

Integrated Rate Equation and Half-Life

Order	Integrated rate equation	Half-life $t_{1/2}$
0	$[A]_t = -kt + [A]_0$	$[A]_0 / 2k$
1	$\ln[A]_t = -kt + \ln[A]_0$	$0.693/k$
2	$1/[A]_t = kt + 1/[A]_0$	$1/k[A]_0$
3	$kt = \frac{1}{[A]_0 - 2[A]_t} \ln \frac{[A]_0[A]_t}{[A]_t[A]_0}$	-
n	$(n-1)kt = \frac{1}{[A]^n - 1} - \frac{1}{[A]_0^n - 1}$	$\frac{2^n - 1}{k(n-1)[A]_0^{n-1}}$

- Relationship between times for different fractions of a first order reaction to complete:  
 $t_{3/4} \text{ or } t_{75\%} = 2t_{1/2}$   
 $t_{7/8} \text{ or } t_{87.5\%} = 3t_{1/2}$   
 $t_{15/16} \text{ or } t_{93.75\%} = 4t_{1/2}$   
 $t_{31/32} \text{ or } t_{96.875\%} = 5t_{1/2}$   
 $t_{63/64} \text{ or } t_{98.4375\%} = 6t_{1/2}$

Temperature Dependence of Rate of Reaction and Effect of Catalyst

- **Arrhenius equation:**  $k = Ae^{-E_a/RT}$   
or  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$
- **Activation energy**  
= Threshold energy - Average kinetic energy of reactants
- **Collision theory:**  $k = PZ e^{-E_a/RT}$   
where P is steric factor and Z is collision frequency.
- **Catalyst** increases the rate of a reaction without itself undergoing any permanent chemical change.

HAVE A LOOK!

- Different solutions having same vapour pressure are called **isopiestic solutions**.
- **Deliquescent** substances absorb moisture because vapour pressure of their saturated solutions is less than that of water vapours in air at that temperature.
- **Fluorescent** substances lose their water of crystallisation because their hydrated crystals have vapour pressure larger than that of water vapours in air.
- Association generally occurs in non-aqueous solvents (non-polar) because high dielectric constant of water helps in the dissociation of the associated molecules.