

- Relative Lowering of v.p :** In terms of molecular weight of solute

$$\frac{P^\circ - P_s}{P^\circ} = \chi_A = \frac{n_A}{n_A + n_B} \quad M_A = \frac{W_A \times M_B}{W_B \left[\frac{P^\circ - P_s}{P^\circ} \right]}$$

Where, P° & P_s = vapour pressure of pure solvent and solution
 n_A, n_B = moles of solute & solvent
 W_A, W_B & M_A, M_B = W_A, W_B are the masses and M_A, M_B are the molar masses of the solute and solvent respectively.

- Elevation in b.p.** $\Delta T_b = K_b m$
 K_b = boiling point elevation constant or molal elevation constant (**ebullioscopic constant**) having unit $K \text{ kg mol}^{-1}$

$$m = \text{molality} \left[m = \frac{W_A}{M_A \times W_B} \times 1000 \right]; \Delta T_b = \frac{K_b W_A}{M_A \times W_B} \times 1000$$

$$\Delta T_b = T_s - T_b$$

T_s & T_b are the boiling point of solution and pure solvent.

- Depression in f.p.** $\Delta T_f = K_f m$
 K_f = freezing point depression constant or molal depression constant or **cryoscopic constant**.

$$\Delta T_f = \frac{K_f W_A}{M_A \times W_B} \times 1000 \quad ; \quad \Delta T_f = T_f - T_s$$

T_s & T_f are the freezing point of solution and pure solvent.
 The values of K_f and K_b , which depend upon nature of the solvent can be determined from the following relations.

$$K_f = \frac{M_B R T_f^2}{1000 \Delta_{\text{fus}} H} \quad ; \quad K_b = \frac{M_B R T_b^2}{1000 \Delta_{\text{vap}} H}$$

Here, R & M_B stand for the gas constant and molar mass of solvent in $\text{g} \cdot \text{mol}^{-1}$, T_f & T_b = freezing point and the boiling point. $\Delta_{\text{fus}} H$ & $\Delta_{\text{vap}} H$ = enthalpies for the fusion and vaporisation of the solvent, respectively.

Colligative properties:

These properties of a solution depend on the total concentration of all solute particles, regardless of their ionic or molecular nature, charge, or size.

- $\propto$ No. of particles
- $\propto$ No. of molecules (In the solution of non-electrolytes)
- $\propto$ No. of ions (In the solution of electrolytes)

SOLUTIONS

Osmotic Pressure (π):

- Osmotic pressure is the hydrostatic pressure produced when a solution is separated from the solvent by a semipermeable membrane.
- Osmotic pressure may be defined as the excess pressure which must be applied to a solution order to prevent flow of solvent into the solution through the semipermeable membrane.

$$\text{Osmotic pressure } (\pi) = \frac{n}{V} RT = CRT$$

For dilute solutions, osmotic pressure is found to follow the equation $(\pi) = \frac{n}{V} RT = CRT$ (Gay-Lussac-van't Hoff law)

when w g of solute are dissolved in V litre of solutions and M is the molar mass of the solute, then $(\pi) = \frac{wRT}{MV} \left[\because n = \frac{w}{M} \right]$

van't Hoff Factor (i)

Certain solutes which undergo dissociation or association in solutions are found to show abnormal molecular mass. Thus, in order to know about the extent of association or dissociation of solutes in solution van't Hoff in 1886 introduced a factor (i). It is defined as the ratio of the normal mass to the observed molecular mass of the solute i.e.

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} \quad ; \quad \text{since, molecular mass} \propto \frac{1}{\text{Colligative property}}$$

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}} \quad \therefore i = \frac{\text{Total number of particles after association/dissociation}}{\text{No. of particles before association/dissociation}}$$

The value of i depends upon the state of solute in the solution. Following cases may become possible.

- when $i = 1$, then the solute remains unaffected (i.e., normal) in solution.
- when $i > 1$, then the solute undergoes dissociation in solution.
- when, $i < 1$, then the solute undergoes association in solution.

Modified equation for colligative properties.

$$\frac{P^\circ - P_s}{P^\circ} = i \chi_A = \frac{n_A}{n_A + n_B}; \Delta T_b = i K_b m; \Delta T_f = i K_f m; \quad \pi = i \frac{n}{V} RT$$

Solubility: Maximum amount of a substance that can be dissolved in a specified amount of solvent at a specified temperature it depends upon

- Nature of solute
- Nature of solvent
- Temperature
- Pressure

Solubility of a solid in liquid

- Effect of nature of solute and solvent $\Rightarrow$ like dissolves like
- Effect of temp $\Rightarrow$ Exothermic process - increase with rise in temp.
- Endothermic process - decrease with rise in temp.
- Effect of pressure $\Rightarrow$ No effect

Solubility of a gas in liquid

- Effect of temp. $\Rightarrow$ Follow same order as in case of solid.
- Effect of pressure $\Rightarrow$ Henry's law states that the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution" $p = K_H x$
- $K_H \Rightarrow$ Henry's law constant solubility $\propto \frac{1}{K_H}$

Raoult's Law

$$(P_s = P_A^\circ + (P_B^\circ - P_A^\circ) x_B)$$

$$P_s = P_A^\circ + (P_B^\circ + P_A^\circ) x_B \text{ where}$$

P_s = Total pressure,
 P_A° & P_B° = vapour pressure in pure state of two constituents A and B in solution

Types of solution

Classification based on physical state:

- Gas in gas (Air)
- Gas in liquid (Soda water)
- Gas in solid (Hydrogen in Pd)
- Liquid in gas (Fog)
- Liquid in liquid (Alcohol in water)
- Liquid in solid (Amalgams)
- Solid in gas (Smog)
- Solid in liquid (Sugar in water)
- Solid in solid (Alloys)

Classification based on concentration

- Dilute solutions
- Concentrated solutions
- Saturated solutions
- Supersaturated solutions

Non-ideal solutions

Ideal solution	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
(i) Obey Raoult's law at every range of concentration.	(i) Do not obey Raoult's law.	(i) Do not obey Raoult's law.
(ii) $\Delta V_{\text{mix}} = 0$; total volume of solution is equal to the sum of volumes of the components.	(ii) $\Delta V_{\text{mix}} > 0$. Volume is increased after dissolution.	(ii) $\Delta V_{\text{mix}} < 0$. Volume is decreased during dissolution.
(iii) $\Delta H_{\text{mix}} = 0$; neither heat is evolved nor absorbed during dissolution.	(iii) $\Delta H_{\text{mix}} > 0$. Endothermic dissolution; heat is absorbed.	(iii) $\Delta H_{\text{mix}} < 0$. Exothermic dissolution; heat is evolved.
(iv) A - A, A - B, B - B molecular interactions present in the two liquids should be same, i.e., A and B are identical in shape, size and character.	(iv) A - B force of attraction are less than A - A and B - B attractive forces. A and B have different shape, size character.	(iv) A - B force of attraction are greater than A - A and B - B attractive forces. A and B also have different shape, size and character.
(v) $P_{\text{Total}} = P_A + P_B = P_A^\circ x_A + P_B^\circ x_B$ i.e., $P_A = P_A^\circ x_A$; $P_B = P_B^\circ x_B$	(v) $P_A > P_A^\circ x_A$; $P_B > P_B^\circ x_B$ $\therefore P_{\text{Total}} > P_A^\circ x_A + P_B^\circ x_B$	(v) $P_A < P_A^\circ x_A$; $P_B < P_B^\circ x_B$ $\therefore P_{\text{Total}} < P_A^\circ x_A + P_B^\circ x_B$
(vi) Escaping tendency of A and B is same in pure liquids as well as in the solution	(vi) Escaping tendency of A and B is very high (showing higher vapour pressure than expected)	(vi) Due to lower escaping tendency it shows lower vapour pressure than expected
Examples Dilute solutions Ethyl bromide + Ethyl iodide n-Butyl chloride + n-Butyl bromide	Examples Acetone + Ethanol $\text{CCl}_4 + \text{CHCl}_3$	Examples Acetone + Aniline Chloroform + Diethyl ether

Concentration of solutions

- Mass percentage (w/W) = $\frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$
- Molarity (M) = $\frac{\text{No. of moles of solute}}{\text{Volume of solution (L)}}$
- Molality (m) = $\frac{\text{No. of moles of solute}}{\text{Weight of the solvent in kg}}$
- Normality (N) = $\frac{\text{No. of grams equivalent of solute}}{\text{Volume of solution (L)}}$
- Mole fraction (x) = $\frac{\text{No. of moles of solute}}{\text{Total moles in solution}}$
- Volume percentage (v/V) = $\frac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$
- ppm = $\frac{\text{No. of parts of solute}}{\text{Total no. of parts of all components of solution}} \times 10^6$
- Mass by volume percentage (w/V) = $\frac{\text{mass of solute}}{\text{Total volume of solution (mL)}} \times 100$
- Mass %, ppm, mole fraction and molality are independent of**