

## Solutions

True solution: A homogeneous mixture. Ex: Soln. = solute + solvent

Colligative properties: Properties which depends on no. of solute particles dissolved in known volume of a given solvent.

- 1) Independent on nature of solute, depends on nature of solvent.
- 2) Applicable for dil. soln. containing non-volatile solute only.
- 3) Colligative properties  $\propto \frac{1}{\text{G.M.Wt of solute}}$

They are

- Ⓐ Relative Lowering of Vapour Pressure of soln. (RLVP)
- Ⓑ Elevation in the boiling point of soln. ( $\Delta T_b$ )
- Ⓒ Depression in the freezing point of soln. ( $\Delta T_f$ )
- Ⓓ Osmotic Pressure ( $\pi$ ).

Lowering of vapour pressure (L.V.P): When a non-volatile solute is added to pure solvent vapour pressure of solvent decreases.  
 → Entropy ( $\Delta S$ ) is higher for soln. than pure solvent. Soln has lower tendency to vapourise.

$$\boxed{L.V.P = P_0 - P_s}$$

$P_0 = \text{v.p of pure solvent}$   
 $P_s = \text{v.p of soln.}$

$$R.L.V.P = \frac{L.V.P}{P_0} = \frac{P_0 - P_s}{P_0}$$

→ It has no units, at any temp. v.p ↓ with ↑ in conc. of soln.

Raoult's law:  $\boxed{R.L.V.P = \text{mole fraction of solute}}$

$$\frac{P_0 - P_s}{P_0} = X_{\text{solute}} = \frac{n_s}{n_s + n_0}$$

$n_s = \text{no. of moles of solute}$   
 $n_0 = \text{no. of moles of solvent}$

for very dil. soln. →  $\frac{P_0 - P_s}{P_0} = \frac{n_s}{n_0}$

If  $H_2O$  is taken as pure solvent then its vapour pressure is 760 mm Hg = 760 mm Hg = 1 bar

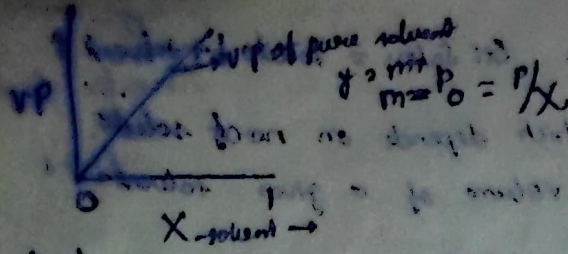
$$n_s = \frac{\text{wt. of solute (a)}}{\text{G.W.T of solute (M)}} \quad n_0 = \frac{\text{wt. of solvent (b)}}{\text{G.W.T of solvent (W)}}$$

$$\frac{P_0 - P_s}{P_0} = \frac{a}{M} \times \frac{W}{b}$$

$$\boxed{n_s = a/M}$$

$$\boxed{n_0 = b/W}$$





Applicable for  
 → det. soln. of non volatile solute only  
 → when solute & solvent form ideal soln.  
 → accurate.  
 → applicable for ideal soln.

Equimolar soln in same solvent will have same b.p & m.p.

### Concentration methods of soln.

① Molarity (M):  $M = \frac{\text{no. of moles of solute (n)}}{\text{Vol. of soln. (in L)}} = \frac{n}{V_{\text{soln.}}} \times 1000 = \frac{(1. w\%) \times 10}{\text{GMW of solute}} = \frac{(2. w\%) \times 10}{\text{GMW of solute}}$

$M = \frac{x \times d \times 10}{\text{GMW}} = \frac{x \times \text{SPG} \times 10}{\text{GMW}}$  (x = % w/w, d = density, SPG = specific gravity)

→ Molarity of pure water = 55.5 M

Molarity depends on temperature (T) ( $M \propto 1/T$ )

→ Decimolar solution =  $M/10 = 0.1 M$   
 centimolar soln. =  $M/100 = 0.01 M$   
 millimolar soln. =  $\frac{M}{1000} = 0.001 M$   
 Decamolar soln. = 10 M  
 hemimolar soln. =  $M/2 = 0.5 M$

→ dilution law  $\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$   
 $M_{\text{resulting}} = \frac{M_1 V_1 + M_2 V_2 + \dots}{V_{\text{total}}}$

② Molality (m):  $m = \frac{\text{no. of moles of solute (n)}}{\text{wt. of solvent (in kg)}} = \frac{n}{\text{GMW (g)}} \times 1000$

$m = \frac{x}{(100-x)} \times \frac{1000}{\text{GMW}} \left[ x_2 \% (w/w) \right]$

$m = \frac{\text{solubility} \times 10}{\text{Mol wt of solute}}$

molality (m) =  $\frac{1000 \times M}{(1000 \times d) - (M \times M_2)}$  → Molality

③ Mole fraction (X)  $\Rightarrow X_{n_1} = \frac{n_1}{n_1 + n_2 (\text{total})}$   $X_{n_1} + X_{n_2} = 1$

$X_{\text{solute}} = \frac{m}{m + \frac{1000}{\text{GMW (solvent)}}} = \frac{M \times M_1}{M(M_1 - M_2) + d}$  (M = molarity, d = density)



Solubility factors are

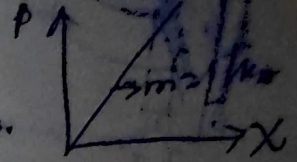
- i) Nature of gas
- ii) Nature of solvent
- Temperature
- Pressure

Henry law: i)  $m = K \cdot P$

mass of gas = m  
conc

ii)  $P = K_H \cdot X_{gas}$

$K_H$  = Henry's const.

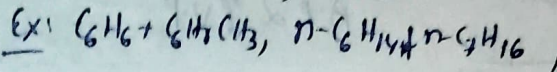


Ideal soln soln obey Raoult's law

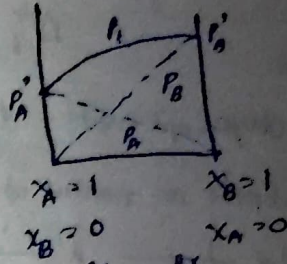
$\Delta H_{mix} = 0, \Delta V_{mix} = 0, P_A = P_A^0 X_A$

$\Delta G_{mix} < 0, \Delta S_{mix} > 0, \Delta S_{neq} = 0$

→ A-A + B-B (interactions) are made.



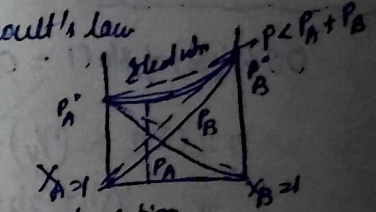
$P_{total} = P_A^0 X_A + P_B^0 X_B$



Non-ideal soln soln which don't obey Raoult's law

→ A-B interactions are more

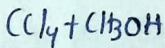
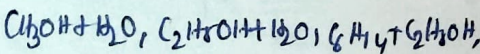
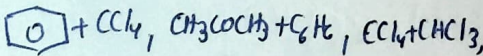
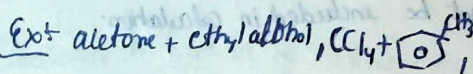
$P_{total} < P_A^0 X_A + P_B^0 X_B$



+ve deviation

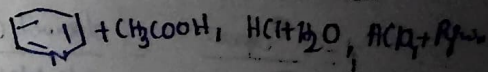
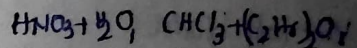
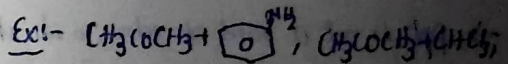
$\Delta H_{mix} > 0, \Delta V_{mix} > 0, P_A > P_A^0 X_A, P_B > P_B^0 X_B$

$\Delta G_{mix} < 0, \Delta S_{mix} < 0, \Delta S_{neq} > 0, \Delta S_{neq} < 0$



$\Delta H_{mix} < 0, \Delta V_{mix} < 0, P_A < P_A^0 X_A, P_B < P_B^0 X_B$

$\Delta G_{mix} > 0, \Delta S_{mix} < 0, \Delta S_{neq} < 0, \Delta S_{neq} > 0$



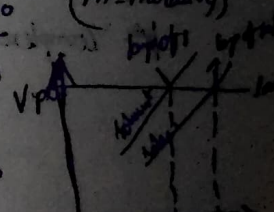
Vapour pressure of soln  $P_{total} = P_B^0 + (P_A^0 - P_B^0) X_A$

$P_A = Y_A P_{total} \Rightarrow P_A^0 X_A = Y_A P_{total} \Rightarrow P_B^0 (1 - X_A) = Y_B P_{total}$

Elevation in b.p ( $\Delta T_b$ ): ebullioscopic const.

$T_b^S - T_b^0 = \Delta T_b, \Delta T_b = K_b X = K_b m = \frac{K_b \times W_B \times 1000}{M_B \times W_A}$  (m = molality)

$\Delta T_b = \frac{RT_b^2}{\Delta H_{vap}} X = \frac{RT_b^2}{w \times L_v} X = \frac{RT_b^2}{L_v \times 1000}$

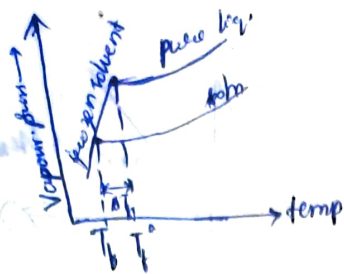


$K_b (H_2O) = 0.52 \text{ K kg mol}^{-1}$

$\Delta T_b = i \times K_b \times \left( \frac{a}{M} \times \frac{1000}{b} \right)$

→ Colligative method used for determination of molar mass of solute using elevation of b.p.

## Depression in freezing point ( $\Delta T_f$ ):



$$\Delta T_f = K_f \cdot m = \frac{RT_0^2}{\Delta H_f} \chi = \frac{RT_0^2}{i_f \times 1000}$$

$$\Delta P \propto \Delta T$$

$$K_f = 1.86 \text{ K kg mol}^{-1} \text{ for } H_2O, \quad K_f = \frac{RT_0^2 M}{\Delta H_f \times 1000} = \frac{RT_0^2 M}{i_f \times 1000}$$

$$m = \frac{w/M}{b/1000}$$

$$\Delta T_f = i \times K_f \times m = i \frac{K_f \times w \times 1000}{b \times M}$$

$K_f$  - cryoscopic const. depends on chemical nature of solvent & independent on nature of solute.

$$B.P \propto \sqrt[3]{V.P}$$

$$F.P \propto \frac{1}{\text{no. of ions}} \propto \frac{1}{\text{no. of solute particles}}$$

## Osmotic pressure ( $\pi$ ): $\pi = \rho gh$

0.9% (w/v) of NaCl = 0.16 M of NaCl = normal saline is isotonic with blood

$$\pi = CRT = (\pi/v) RT = \left( \frac{a}{M} \times \frac{1}{V} \right) RT$$

$$\pi = \frac{(n_1 i_1 + n_2 i_2 + \dots) RT}{V}, \quad \pi_{\text{total}} = \frac{(\pi_1 V_1 + \pi_2 V_2 + \dots)}{V_1 + V_2 + \dots}$$

$$\pi_{\text{total}} = \frac{(n_1 i_1 + n_2 i_2 + \dots) RT}{V_{\text{total}}}$$

→ ppt is not a part of soln, so it should not be included in calculation.

→ Vant Hoff's factor

$$i = \frac{\pi_{\text{experi}}}{\pi_{\text{calculated}}} = \frac{\text{observed CP}}{\text{calculated CP}}$$

$$\text{for dissociation} - \alpha = \frac{i-1}{n-1}$$

$n$  = no. of ions

$$\text{for association} - \alpha = \frac{i-1}{1-1/n} \text{ (or) } \frac{i-1}{1/n-1}$$

for non-electrolyte  $i=1$ , for strong electrolyte  $i=n$

