8.SOLUTION & COLLIGATIVE PROPERTIES

1.. **OSMOTIC PRESSURE :**

(i) $\pi = \rho gh$

Where, ρ = density of soln., h = equilibrium height.

(ii) **Vont – Hoff Formula** (For calculation of O.P.)

$$\pi = CST$$

$$\pi = CRT = \frac{n}{V} RT$$ (just like ideal gas equation)

$\therefore$ C = total conc. of all types of particles.

$= C_1 + C_2 + C_3 + \ldots\ldots\ldots\ldots\ldots\ldots$

$$= \frac{(n_1 + n_2 + n_3 + \ldots\ldots\ldots)}{V}$$

Note : If V_1 mL of C_1 conc. + V_2 mL of C_2 conc. are mixed.

$$\pi = \left(\frac{C_1V_1 + C_2V_2}{V_1 + V_2}\right)RT \quad ; \quad \pi = \left(\frac{\pi_1V_1 + \pi_2V_2}{RT}\right)$$

Type of solutions :

(a) Isotonic solution – Two solutions having same O.P.

$\pi_1 = \pi_2$ (at same temp.)

(b) Hyper tonic– If $\pi_1 > \pi_2$. $\Rightarrow$ I^{st} solution is hypertonic solution w.r.t. 2^{nd} solution.

(c) Hypotonic – II^{nd} solution is hypotonic w.r.t. I^{st} solution.

Abnormal Colligative Properties : (In case of association or dissociation)

VANT HOFF CORRECTION FACTOR (i) :

$$i = \frac{\text{exp/observed/actual/abnormal value of colligative property}}{\text{Theoritical value of colligative property}}$$

$$= \frac{\text{exp./observed no. of particles / conc.}}{\text{Theoritical no. of particles}} = \frac{\text{observed molality}}{\text{Theoritical molality}}$$

$$= \frac{\text{theoretical molar mass (formula mass)}}{\text{experimental / observed molar mass (apparent molar mass)}}$$

- $i > 1$ $\Rightarrow$ dissociation.
  $i < 1$ $\Rightarrow$ association.

- $$i = \frac{\pi_{exp.}}{\pi_{theor}}$$

$\therefore \pi = iCRT$

$\pi = (i_1C_1 + i_2C_2 + i_3C_3.....)\, RT$

Relation between i & α (degree of dissociation) :

$i = 1 + (n - 1)\alpha$ **Where,** $n = x + y$.

Relation b/w degree of association β & i.

$$i = 1 + \left(\frac{1}{n} - 1\right)\beta$$

2. RELATIVE LOWERING OF VAPOUR PRESSURE (RLVP) :

Vapour pressure : $P_{Soln.} < P$

Lowering in VP $= P - P_s = \Delta P$

Relative lowering in vapour pressure $\text{RLVP} = \frac{\Delta P}{P}$

Raoult's law : – (For non – volatile solutes)

Experimentally relative lowering in V.P = mole fraction of the non volatile solute in solutions.

$$\text{RLVP} = \frac{P - P_s}{P} = X_{Solute} = \frac{n}{n+N}$$

$$\boxed{\frac{P - P_s}{P_s} = \frac{n}{N}}$$

$$\boxed{\frac{P - P_s}{P_s} = (\text{molality}) \times \frac{M}{1000}}$$

(M = molar mass of solvent)

If solute gets associated or dissociated

$$\frac{P - P_s}{P_s} = \frac{i.n}{N}$$

$$\frac{P - P_s}{P_s} = i \times (\text{molality}) \times \frac{M}{1000}$$

- According to Raoult's law
  (i) $p_1 = p_1^0 X_1$. where X_1 is the mole fraction of the solvent (liquid).
  (ii) An alternate form → $\frac{p_1^0 - p_1}{p_1^0} = X_2$.

- **Ostwald–Walker Method : Experimental or lab determination of $\frac{\Delta P}{P}$ or $\frac{\Delta P}{P_S}$**

$$\frac{P - P_s}{P_s} = \frac{\text{loss in wt. of solvent}}{\text{loss in wt. of solution}}$$

$$\frac{P - P_s}{P} = \frac{\text{loss in wt. of solvent}}{\text{gain in wt. of dehydrating agent}}$$

3. ELEVATION IN BOILING POINT :

$\Delta T_b = i \times K_b m$

$$K_b = \frac{RT_b^2}{1000 \times L_{vap}} \quad \text{or} \quad K_b = \frac{RT_b^2 M}{1000 \times \Delta H_{vap}}$$

$$L_{vap} = \left(\frac{\Delta H_{vap}}{M}\right)$$

4. DEPRESSION IN FREEZING POINT :

$\therefore \Delta T_f = i \times K_f . m.$

$$K_f = \text{molal depression constant} = \frac{RT_f^2}{1000 \times L_{fusion}} = \frac{RT_f^2 M}{1000 \times \Delta H_{fusion}}.$$

RAOULT'S LAW FOR BINARY (IDEAL) MIXTURE OF VOLATILE LIQUIDS :

$\mathbf{P_A = X_A P_A^0}$ ∴ $\mathbf{P_B = X_B P_B^\circ}$

if $P_A^\circ > X_B^\circ$ ∴ A is more volatile than B

∴ B.P. of A < B.P. of B

∴ According to Dalton's law

$\mathbf{P_T = P_A + P_B = X_A P_A^0 + X_B P_B^0}$

x_A' = mole fraction of A in vapour about the liquid / solution.

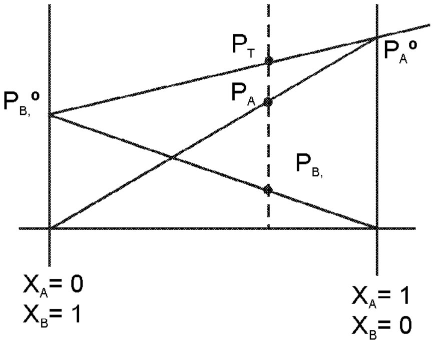
x_B' = mole fraction of B

$$\mathbf{P_A = X_A P_A^\circ = X_A' P_T}$$

$$\mathbf{P_B = X_B' P_T = X_B P_B^0}$$

$$\frac{1}{P_T} = \frac{x_A'}{P_A^0} + \frac{x_B'}{P_B^0}.$$

Graphical Representation :



A more volatile than B ($P_A^o > P_B^o$)

Ideal solutions (mixtures) :

Mixtures which follow Raoul'ts law at all temperature.

A ------ A $\Rightarrow$ A -------- B,
B ----- B

$\Delta H_{mix} = 0$: $\Delta V_{mix} = 0$: $\Delta S_{mix} = +$ ve as for process to proceed : $\Delta G_{mix} = -$ ve

eg. **(1) Benzene + Toluene.**
(2) Hexane + heptane.
(3) $C_2H_5Br + C_2H_5I$.

Non - Ideal solutions :

Which do not obey Raoult's law.

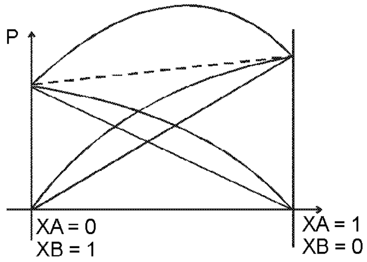
(a) Positive deviation : –

(i) $P_{T,exp} > (X_A P^o_A + X_B P_B^o)$

(ii) $\begin{matrix} A----A \\ B----B \end{matrix} > A ---- B$
$\downarrow$
Weaker force of attraction

(iii) $\Delta H_{mix} = +ve$ energy absorbed
(iv) $\Delta V_{mix} = +ve$ (1L + 1L > 2L)
(v) $\Delta S_{mix} = +ve$
(vi) $\Delta G_{mix} = -ve$

eg. **$H_2O + CH_3OH$.**
$H_2O + C_2H_5OH$
C_2H_5OH + hexane
C_2H_5OH + cyclohexane.
$CHCl_3 + CCl_4 \rightarrow$ dipole dipole interaction becomes weak.



$P^0A > P^0B$

(b) **Negative deviation**

(i) $P_T \text{ exp} < x_A p^o + x_B p^o_B$

(ii) $\begin{matrix} A - - - - A \\ B - - - - B \end{matrix} > A ------ B.$

strong force of altraction.

(iii) $\Delta H_{mix} = -ve$

(iv) $\Delta V_{mix} = -ve$ (1L + 1L < 2L)

(v) $\Delta S_{mix} = +ve$

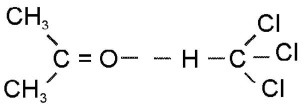
(vi) $\Delta G_{mix} = -ve$

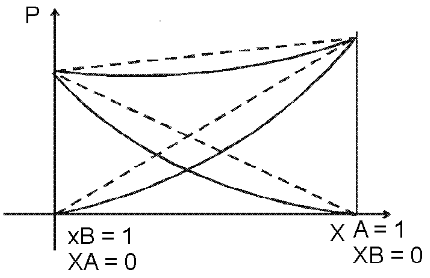
eg. **$H_2O + HCOOH$**

$H_2O + CH_3COOH$

$H_2O + HNO_3$

$CHCl_3 + CH_3OCH_3$ ⇒





$P^0A > P^0B$

Immiscible Liquids :

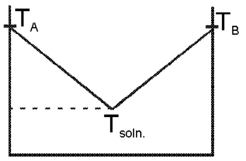
(i) $P_{total} = P_A + P_B$

(ii) $P_A = P_A{}^0 X_A = P_A{}^0$ [Since, $X_A = 1$].

(iii) $P_B = P_B{}^0 X_B = P_B{}^0$ [Since, $X_B = 1$].

(iv) $P_{total} = P_A{}^0 + P_B{}^0$ (v) $\frac{P_A^0}{P_B^0} = \frac{n_A}{n_B}$ (vi) $\frac{P_A^0}{P_B^0} = \frac{W_A M_B}{M_A W_B}$

$P_A{}^0 = \frac{n_A RT}{V}$; $P_B{}^0 = \frac{n_B RT}{V}$



B.P. of solution is less than the individual B.P.'s of both the liquids.

Henry Law :

This law deals with dissolution of gas in liquid i.e. mass of any gas dissolved in any solvent per unit volume is proportional to pressure of gas in equilibrium with liquid.

$m \ \alpha \ p$

$m = kp$

$m \rightarrow \frac{\text{weight of gas}}{\text{Volume of liquid}}$