CHAPTER

2 Solution

Vapour Pressure

Pressure exerted by vapours over the liquid surface at equilibrium.

$T\uparrow \Rightarrow$ V.P.$\uparrow$

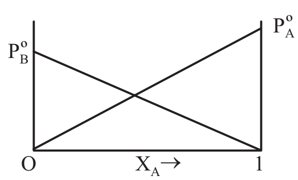
Attractive Forces$\uparrow \Rightarrow$ V.P. $\downarrow$

Raoult's Law

(1) Volatile binary liquid mix:

Volatile liq.	A	B
Mole fraction	X_A / Y_A	$X_B / Y_B \Rightarrow$ liq/vapour
V.P. of pure liq.	P_A°	P_B°

Binary liquid solution:



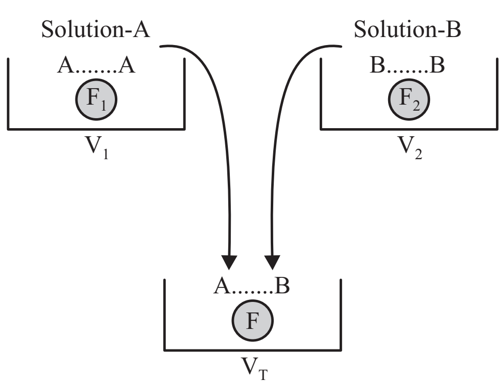
By Raoult's law $\Rightarrow$ $P_T = P_A^\circ X_A + P_B^\circ X_B = P_A + P_B$ ...(*i*)

By Dalton's law $\Rightarrow$ $P_A = Y_A P_T$ ...(*ii*)

$P_B = Y_B P_T$ ...(*iii*)

Ideal and Non-Ideal Solutions

Ideal Solutions



Ideal solution : $\begin{cases} F_1 \simeq F_2 \simeq F \\ V_T = V_1 + V_2 \end{cases} \Rightarrow \Delta H_{solution} = 0$

Non-Ideal Solutions

(1) Solution showing +ve deviation :

$F < F_1$ or F_2

$V_T > V_1 + V_2$

$\because$ $\Delta H_{solution} > 0$

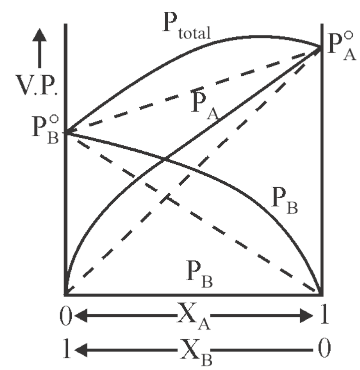


Fig.: A solution that shows +ve deviation from Raoult's law

(2) Solution showing -ve deviation:

$\Rightarrow F > F_1$ and F_2

$\Rightarrow V_T < (V_1 + V_2)$

$\Rightarrow \Delta H_{solution} < 0$

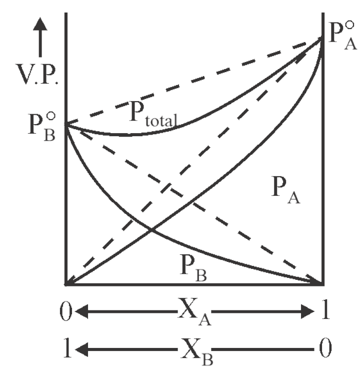


Fig.: A solution that shows -ve deviation from Raoult's law

Table: Deviation from Raoult's Law

	Positive deviation (ΔH = +ve)	Negative deviation (ΔH = – ve)	Zero deviation (ΔH = 0)
(*i*)	ethanol + cyclohexane	acetone + chloroform	benzene + toluene
(*ii*)	acetone + carbon disulphide	benzene + chlorform	n-hexane + n-heptane
(*iii*)	acetone + benzene	nitric acid + chloroform	ehyl bromide + ethyl iodide
(*iv*)	ethanol + acetone	acetone + aniline	chlorobenzene + bromo benzene
(*v*)	ethanol + water	water + nitric acid	
(*vi*)	carbon tetrachloride + chloroform	diethyl ether + chloroform	

Azeotropic mixtures: Some liquids on mixing in a particular composition form azeotropes which are binary mixture having same composition in liquid and vapour phase and boil at a constant temperature. Azeotropic mixture cannot be separated by fracional distillation.

Types of Azeotropic Mixtures

(*i*) **Minimum boiling Azeotropic mixtures:** The mixture of two liquids whose boiling point is less than either of the two pure components. They are formed by non-ideal soluton showing positive deviation. For example ethanol (95.5%) + water (4.5%) water boils at 351.15 K.

(*ii*) **Maximum boiling Azeotropic mixtures:** The mixture of two liquids whose boiling point are more than either of the two pure components. They are formed by non-ideal solutions showing negative deviation. For example HNO_3 (68%) + water (32%) mixture boils at 393.5 K.

Colligative Properties

Properties depends on relative no. of particles of non volatile solute in solution.

No. of particle of Non volatile solute $\uparrow \Rightarrow$ Colligative Properties $\uparrow$

(1) Relative lowering of V.P. :

$$\frac{P_A^\circ - P_A}{P_A^\circ} = i\frac{n_B}{n_A + n_B} \simeq i\frac{n_B}{n_A} \text{ [For dilute solution]}$$

where n_B = mole of Non-volatile solute.

i = Van't Hoff's factor.

(2) Elevation in B.P. :

$\Delta T_b = (T_b' - T_b) = i.\ K_b \times m.$

where $K_b = \dfrac{RT_b^2}{1000 \times l_v}$

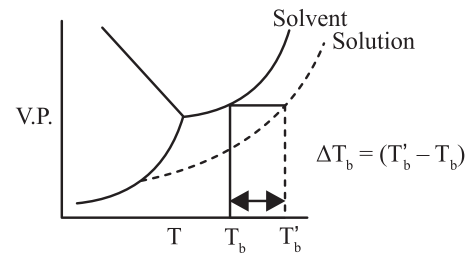
where T_b = B.P. of pure solvent.

l = Latent heat of vapourization (per gm)

K_b = molal elevation constant

M = Molar mass

where $l_v = \left(\dfrac{\Delta H_{vap}}{M}\right)$



(3) Depression in FP:

$\Delta T_f = T_f - T_f' = i\ K_f \times m$

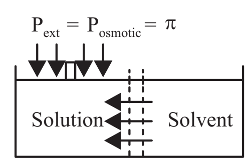
where $K_f = \dfrac{RT_f^2}{1000 \times \ell_f}$

T_f = f.p. of pure solvent

K_f = molal depression constant

l_f = latent heat of fusion per gm.

(4) Osmotic pressure:



$\pi \propto (P_A^\circ - P_A)$

π = iC. R.T.

where π = osmotic pressure

C = molarity (mole/lit)

Sol. (1) Sol (2)

If $\pi_1 = \pi_2$ Isotonic

If $\pi_1 > \pi_2$ $\begin{cases} sol^n (1) \text{ hypertonic} \\ sol^n (2) \text{ hypotonic} \end{cases}$

Table: Van't Hoff factor for different Cases of solutes undergoing Ionisation and Association

Solute	Example	Ionisation/association (x degree)	y*	Van't Hoff factor	Abnormal mol. wt. (m_1')
Non-electrolyte	urea, glucose, sucrose etc.	none	1	1	normal mol.wt.
Ternary electrolyte	K_2SO_4, $BaCl_2$	$\underset{1-x}{A_2B} \rightleftharpoons \underset{2x}{2A^+} + \underset{x}{B^{2-}}$	3	(1 + 2x)	$\frac{m_1}{(1+2x)}$
Electrolyte	$K_3[Fe(CN)_6]$,	$\underset{1-x}{A_3B} \rightleftharpoons \underset{x}{A^{3+}} + \underset{3x}{3B^-}$	4	(1 + 3x)	$\frac{m_1}{(1+3x)}$
Associated Solute	benzoic acid in benzene	$\underset{1-x}{2A} \rightleftharpoons \underset{x/2}{A_2}$	$\frac{1}{2}$	$\left(1-\frac{x}{2}\right)=\left(\frac{2-x}{2}\right)$	$\frac{2m_1}{(2-x)}$
	forming dimer	$\underset{(1-x)}{A} \rightleftharpoons \frac{1}{2}\underset{x/2}{A_2}$	$\frac{1}{2}$	$\left(1-\frac{x}{2}\right)=\left(\frac{2-x}{2}\right)$	$\frac{2m_1}{(2-x)}$
	any solute	$\underset{1-x}{nA} \rightleftharpoons \underset{x/n}{A_n}$	$\frac{1}{n}$	$\left[1+\left(\frac{1}{n}-1\right)x\right]$	$\left[\frac{m_1}{1+\left(\frac{1}{n}-1\right)x}\right]$
	forming polymer A_n	$\underset{(1-x)}{A} \rightleftharpoons \frac{1}{n}\underset{x/n}{A_n}$	$\frac{1}{n}$	$1-x+\frac{x}{n}$	$\frac{m_1}{1-x+\frac{x}{n}}$
General	one mole of solute giving y mol of products	$\underset{1-x}{A} \rightleftharpoons \underset{xy}{yB}$	y	[1 + (y –1)x]	$\frac{m_1}{[1+(y-1)x]}$

*** number of products from one mole of solute**