DILUTE SOLUTIONS

Solution : Homogenous mixture of two or more substances whose composition may be altered within certain limits.

Pre-requisite knowledge

- Basic concentration terms like Molarity, Molality, Mass percentage etc from Some basic concepts of chemistry

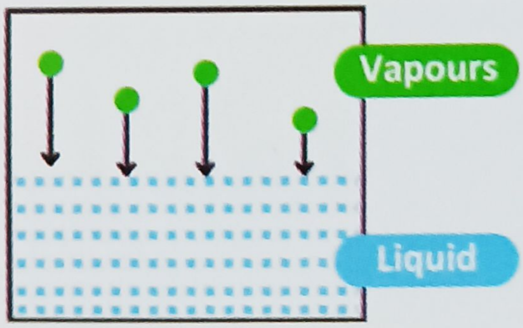
Solubility

$$\text{Solubility} = \frac{\text{Amount of solute dissolved}}{\text{Amount of solvent}} \times 100$$

Types of Liquids

- **Volatile** - Which converts into vapours fast.
- **Non Volatile** - which doesn't convert into vapours.

Vapour Pressure



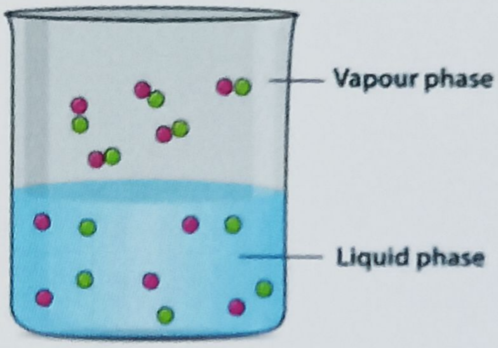
- In closed containers only.

  Liquid $\rightleftarrows$ Vapours
- Pressure exerted by the vapours

VP $\propto$ Temperature

VP $\propto$ 1/Intermolecular forces

Raoult's Law for two volatile liquids

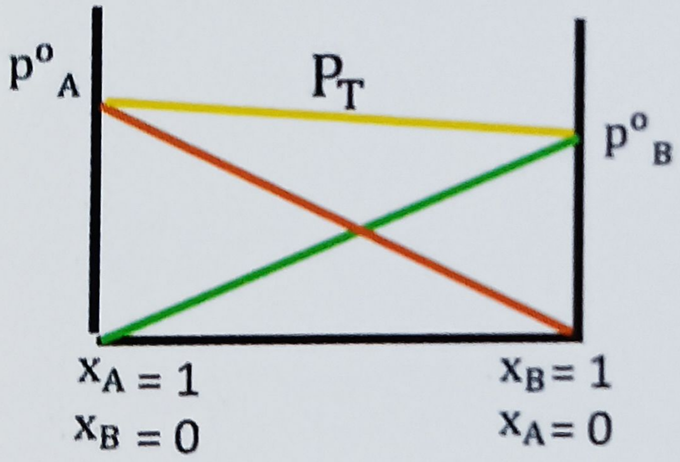


$$p_A = p^o_A \cdot x_A \;\&\; p_B = p^o_B \cdot x_B$$

Total Pressure = $P_T = p_A + p_B$

$$= p^o_A \cdot x_A + p^o_B \cdot x_B$$

p^o_A & p^o_B : Partial vapour pressure of pure A & B
x_A & x_B : Mole fractions in liquid phase
p_A & p_B : Vapour Pressure of A & B in solution



This case is valid when A is more volatile than B

x, here is mole fractions in liquid phase

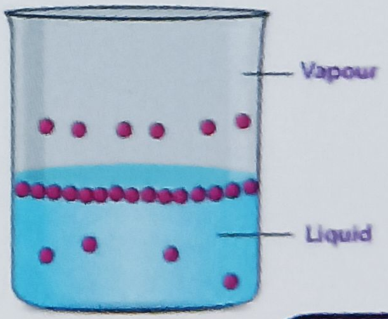
Dalton's Law

if y is mole fractions in gas phase

$$p_A = p^o_A \cdot y_A \;\&\; p_B = p^o_B \cdot y_B$$

Raoult's Law for non volatile solute

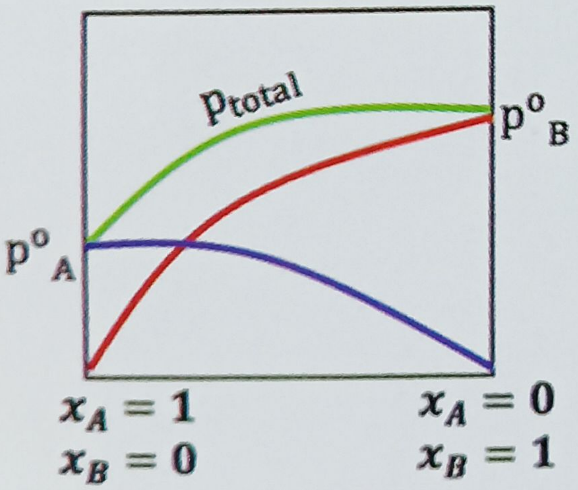
If A is solvent and B is solute, then B doesn't vapourise Thus, $p = 0$



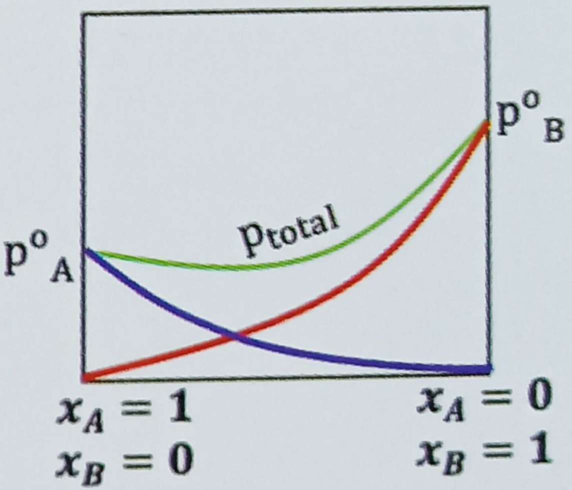
$$P_T = p_A + 0 = p^o_A \cdot x_A$$

$$= p^o_{solvent} \cdot x_{solvent}$$

Ideal Solutions	Ideal and Non-Ideal Solutions	
Obeys Raoult's	Doesn't obey Raoult's Law	
	Positive Deviation	**Negative Deviation**
IMF b/w **A-A and B-B = A-B**	IMF b/w **A-A & B-B > A-B**	IMF b/w **A-A & B-B < A-B**
$p_A = p^o{}_A \cdot x_A$ $p_B = p^o{}_B \cdot x_B$	$p_A > p^o{}_A \cdot x_A$ $p_B > p^o{}_B \cdot x_B$	$p_A < p^o{}_A \cdot x_A$ $p_B < p^o{}_B \cdot x_B$
$\Delta H_{mix} = 0$ $\Delta V_{mix} = 0$ $\Delta S_{mix} > 0$ $\Delta G_{mix} < 0$	$\Delta H_{mix} > 0$ $\Delta V_{mix} > 0$ $\Delta S_{mix} > 0$ $\Delta G_{mix} < 0$	$\Delta H_{mix} < 0$ $\Delta V_{mix} < 0$ $\Delta S_{mix} > 0$ $\Delta G_{mix} < 0$
• Bromoethane + chloroethane • Benzene + Toluene	• $CCl_4 + C_6H_6$ • $CCl_4 + CH_3OH$ • $CCl_4 + C_2H_5OH$ • Ethanol + water	• $HNO_3 + H_2O$ • Acetone + Chloroform • Chloroform + Acetic acid



Positive Deviation



Negative Deviation

Azeotropic mixture

A liquid mixture with a **constant boiling point** and **vapour composition the same as liquid composition.** The components **cannot be se Parated by distillation.**

Minimum Boiling Azeotrope	Maximum Boiling Azeotrope
• B.P. of Azeotrope less than individual Comp.	• B.P. of Azeotrope more than individual Comp.
• Solutions swith Positive deviation from R.L.	• Solutions with Negative deviation from R.L.

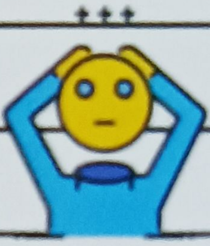
Vant Hoff Factor (*i*)

- Non Electrolytes do not undergo dissociation.
- Electrolytes (Strong or weak) undergo dissociation or association when dissolved in solvent.
- Thus, Actual solute particles differ from theoretical.

For Dissociation	$i > 1$	**For Association**	$i < 1$

$$i = \frac{\text{Actual no. of moles of solute present}}{\text{Theoritical no. moles of solute mixed}}$$

Formula to calculate vant hoff factor when D.O.D (α) is involved	$i = 1 + (n - 1)\alpha$

Value of n in different mechanisms		
Case of Dissociation		
n = 2	$NaCl \rightarrow Na^+ + Cl^-$	Two ions Dissociate
n = 3	$BaCl_2 \rightarrow Ba^{+2} + 2Cl^-$	Three ions Dissociate
Case of Association		
n = 1/2	$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$	

- For Dimerisation, i = 1/2 ; For Trimerisation i = 1/3
- In case of Non-Electrolytes like Glucose,Urea, sucrose, n = 1 resulting in i = 1.
- *i* is included in all the colligative formulas.
- Degree of dissociation is 1 for strong electrolytes

Relative Lowering in Vapour Pressure

On adding non volatile solute to a volatile solvent, the vapour pressure of the solvent **decreases**

P_A^o = partial vapour pressure of Pure solvent
P_s = Partial vapour pressure of solvent in solution

$$\frac{P_A^o - P_s}{P_A^o} = i\,x_B \simeq i\,\frac{n_B}{n_A}$$

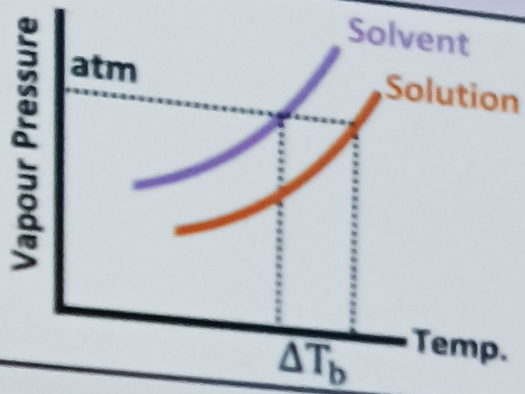
Elevation in Boiling Point

When non volatile solute is dissolved in volatile solvent its V.P decreases. Thus, Boiling point increases

$$\Delta T_b = T_b - T^o_b$$

$$\Delta T_b = iK_b m$$

T_b = Boiling pt. of Solution
T^o_b = Boiling pt. of pure solvent
m = molality of solution
K_b = Ebullioscopic Constant



Ebullioscopic constant

$$K_b = \frac{RT_b^{o2}}{1000\ L_v}$$

K_b(water) = 0.52 K kg/mol

T_b^o = Standard B. P.
L_v = Latent Heat of vap.
$= \frac{\Delta H}{M.W.}$

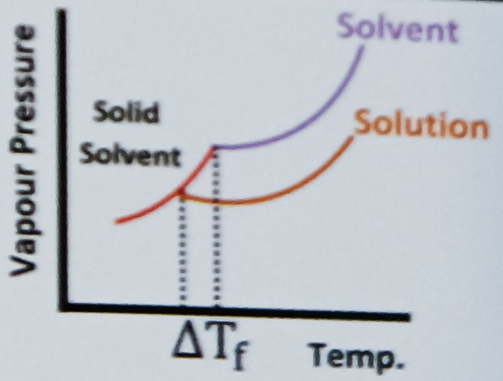
Depression in Freezing Point

When non volatile solute is dissolve in volatile solvent its V.P decreases. Thus, freezing point decreases.

$$\Delta T_f = T^o_f - T_f$$

$$\Delta T_f = iK_f m$$

T_f = Freezing pt. of Solution
T^o_f = Freezing pt. of pure solvent
m = molality of solution
K_f = Cryoscopic Constant



Cryoscopic constant

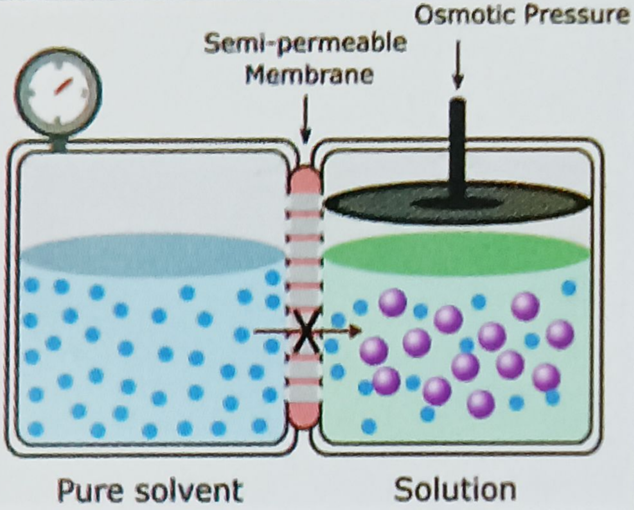
K_f(water) = 1.86 K kg/mol

$$K_f = \frac{RT_f^{o2}}{1000\ L_f}$$

T_f^o = Standard F. P.
L_v = Latent Heat of fus.
$= \frac{\Delta H}{M.W.}$

Osmotic Pressure

The minimum pressure which must be applied on solution side to prevent osmosis



Osmosis only takes place in solutions with different conc.

$$\pi = i\,CRT$$

C = concentration
R = gas constant
T = Absolute Temperature

Types of Solutions

HYPERTONIC	HYPOTONIC	ISOTONIC
		
Solvent diffuses out	Solvent diffuses in	Same osmotic

Henry's Law

The solubility of a gas in a liquid is proportional to pressure of the gas

$$p = K_H . x$$

- Temp ∝ 1/Solubility
- Pressure ∝ Solubility
- K ∝ Temperature

E.g. Bends prevention in scuba drivers

"Whereas the chemico-chemists always find in industry a beautiful field of gold-laden soil, the physico-chemists stand somewhat farther off, especially those who seek only the greatest dilution, for in general there is little to make with watery solutions."

Jacobus Henricus van 't Hoff