CHAPTER - 00
SOLUTIONS

Introduction

- Solutions are homogenous mixtures of two or more than two components.

- The component present usually in largest quantity and does not undergo a phase change is called solute, which is denoted as 1, while the component present in small amount and undergo a phase change is called solute, which is denoted as 2.

- Binary solution - solutions consists of two components only ie., one solute and one solvent.

- Physical state of solution = Physical state of solvent.

Types of Solutions

Depending upon the physical state of solvent taken, solutions are classified into 3 major types

1) Solid solutions

2) Liquid solutions

3) Gaseous solutions

Depending upon the physical state of solute added to a particular solvent, these three major types are further classified into 3 types each so that there are 9 types of solutions.

Solution	Solute	Solvent	Example
Solid solutions	Solid Liquid Gas	Solid	Alloys Amalgam (compounds of Hg) Occluded H_2 in Pd
Liquid solution	Solid Liquid Gas	Liquid	Glucose dissolved in water Ethanol dissolved in water Oxygen dissolved in water
Gaseous solutions	Solid Liquid Gas	Gas	Camphor in Nitrogen gas Chloroform mixed with N_2 gas Mixture of O_2 and N_2

Expressing Concentration of Solution (Concentration Techniques)

Concentration of a solution means the amount of solute in solution. The major concentration techniques are

1. **Mass Percentage (w/w)**

$$(w/w) = \frac{Mass\,of\,one\,component}{Total\,mass\,of\,solution} \times 100$$

10% (w/w) aqueous solution of glucose means 10 g glucose dissolved in 90 g water results in 100 g of glucose solution.

This unit is commonly used in industrial chemical application.

eg : Commercial bleaching solution contains 3.62% (w/w) aqueous solution of sodium hypochlorite.

2. **Volume Percentage (v/v)**

$$v/v = \frac{Volume\,of\,one\,component}{Total\,volume\,of\,solution} \times 100$$

10% (v/v) aqueous solution of ethanol means 10 ml of ethanol dissolved in water such that the total volume of the solution is 100 ml.

This unit is also used in chemical industries

eg : A 35% (v/v) solution of ethylene glycol (anti-freeze) is used in cars for cooling the engine which lowers the freezing point of water to 255.4 K (–17.6^{0}C)

3. **Mass by Volume Percentage (w/v)**

$$w/v = \frac{Mass\,of\,solute}{Volume\,of\,solution\,in\,mL} \times 100$$

5% (w/v) aqueous solution of NaCl means 5g NaCl dissolved in enough water so that the final volume of the solution is 100 ml.

This unit is used in medicine and pharmacy

4. **Parts per million (ppm)**

This unit is commonly used when the solute is present in trace quantities

$$ppm = \frac{Number\,of\,parts\,of\,the\,component}{Total\,number\,of\,parts\,of\,all\,components\,of\,solution} \times 10^6$$

The term 'part' may be mass or volume or both.

In terms of mass,

$$ppm = \frac{Mass\,of\,one\,component}{Total\,mass\,of\,solution} \times 10^2 \times 10^4 = mass\,\% \times 10^4$$

ie ppm = mass % × 10^4

$$\boxed{1ppm = 1mgL^{-1} = 1\mu gmL^{-1}}$$

eg :   1) The level of CO_2 in atmosphere is 0.03% by mass ie., 300 ppm

2) A litre of sea water weighs 1030 g contains 6×10^{-3} g dissolved oxygen. Its concentration is ppm is :

$$\frac{6 \times 10^{-3}}{1030} \times 10^6 = 5.8 \, ppm$$

5.   **Strength(S)**

$$S = \frac{Mass \, of \, solute \, (g)}{Volume \, of \, solution \, (L)} \, gL^{-1}$$

$5gL^{-1}$ aqueous solution of NaCl means 5g NaCl is present in 1 L solution.

6.   **Mole Fraction (χ)**

$$\chi = \frac{Number \, of \, moles \, of \, the \, component}{Total \, number \, of \, moles \, of \, all \, the \, components}$$

For a binary solution

$$\chi_1 = \frac{n_1}{n_1 + n_2} \, and \, \chi_1 = \frac{n_2}{n_1 + n_2}$$

OR $\chi_1 = \dfrac{w_1 / M_1}{w_1 / M_1 + w_2 / M_2} \, and \, \chi_2 = \dfrac{w_2 / M_2}{w_1 / M_1 + w_2 / M_2}$

Also $\chi_1 + \chi_2 = 1$

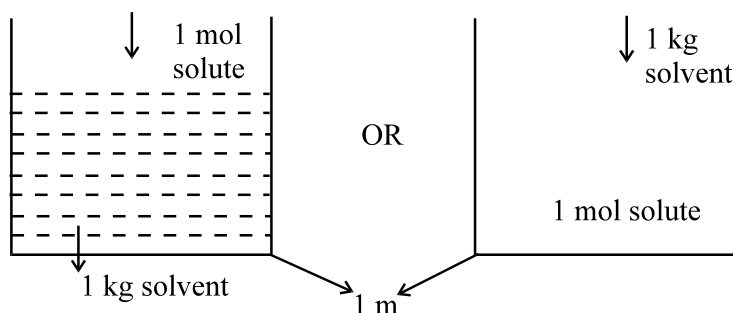Generally, in a given solution sum of all the mole fraction is unity ie.,

$$\chi_1 + \chi_2 + \, ... + \chi_i = 1$$

7.   **Molality (m)**

$$m = \frac{Number \, of \, moles \, of \, solute}{Mass \, of \, solvent \, in \, kg} = \frac{n_2}{w_1} = \frac{w_2}{M_2 . w_1}$$

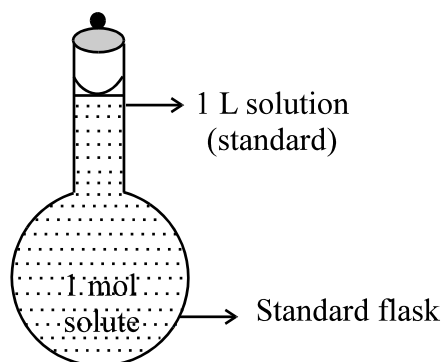If w_1 is in g, $m = \dfrac{w_2 . 1000}{M_2 . w_1} \, mol \, kg^{-1} (m)$

x molal (x m) aqueous solution of NaOH means x mol NaOH dissolved in 1 kg water

8.   **Molality (M)**

$$M = \frac{\text{Number of moles of solute}}{\text{Volume of solution in L}} = \frac{n_2}{V} = \frac{w_2}{M_2.V}$$

x Molar (x M) aqueous solution of NaOH means x mol NaOH present in 1 L solution

→ 1 L solution
  (standard)

1 mol solute → Standard flask

9.   Normality (N)

$$N = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution in L}} = \frac{n_{g-eq}}{V} = \frac{w_2}{E_2.V}$$

E_2 = Equivalent mass of solute

If V is in mL, $N = \dfrac{w_2.1000}{E_2.V} \, eqL^{-1} \, (N)$

x normal (x N) aqueous solution of H_2SO_4 means x g-equivalents of H_2SO_4 present in it solution.

NOTE :

$$\text{Seminormal} = \frac{N}{2} \; ; \qquad \text{Decinormal} = \frac{N}{10} \; \text{etc}$$

10.   **Formality (F)**

$$F = \frac{\text{Number of formula units of solute}}{\text{Volume of solution in L}}$$

This unit is used when the solute is an ionic compound but the magnitude of molecular mass and formula mass of ionic compound is same.

$\therefore F = M$

Some Important Points & Shortcuts

1. $d_{H_2O} = 1 gmL^{-1}$

     $\Rightarrow$ 1 g = 1 mL

              1000 g = 1000 mL

     $\therefore 1 kg H_2O = 1 L H_2O$

     $\therefore$ Number of moles of H_2O in 1L OR $1 kg = \dfrac{1000}{18} = 55.5$ moles

2.   Among the concentration technique ; v/v, w/v, ppm (in terms of volume), S, M, N & F are temperature dependent because volume is included which changes with temperature.

3.   1 molar aqueous solution is more concentrated than 1 molal aqueous solution because less amount of water is present in 1 molar solution.

     But for solvents other than water, m and m are same or different depends upon the density of solvent taken.

4.   If mass % and density of solution (g mL^{-1}) are given,

     $M = \dfrac{10 \times d \times mass \%}{M_2}$

5.   Relation between m and χ

     $m = \dfrac{1000\, \chi_2}{\chi_1 M_1}$

6.   Relation between M and χ

     $M = \dfrac{1000\, d\, \chi_2}{\chi_1 M_1 + \chi_2 M_2}$

7.   Relation between m and M

     $M = \dfrac{1000\, M}{1000\, d - M M_2}$

8.   Relation between N and M

     N = (n-factor) M

          OR

     $n_{eq} = (n - factor) n_{moles}$
                        $\downarrow$
          Acidity of base
          Basicity of acid
          Number of electrons transferred per mole of oxidising agent or reducing agent etc.

9. Molarity Equation

   a) Dilution Formula

   $M_1V_1 = M_2V_2$

   b) Reaction Formula

   $$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

   Here n_1 and n_2 are the stoichiometric coefficients of reactants or products.

10. Normality Equation

   For both dilution and reaction, normality equation is :

   $N_1V_1 = N_2V_2$

   ie., 1 equivalent of reactant A requires 1 equivalent of reactant B

   1 equivalent of reactant A products 1 equivalent of product B

11. Molarity of a Mixture (M_{mini})

   a) Acid + Acid OR Base + Base OR Neutral +Neutral

   $$M_{mix} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

   if $V_1 = V_2$; $M_{mini} = \dfrac{M_1 + M_2}{2}$

   b) Acid + Base

   $$M_{mix} = \frac{M_1V_1 - M_2V_2}{V_1 + V_2}$$

   if $V_1 = V_2$,

   $$M_{mix} = \frac{M_1 - M_2}{2}$$

12. Normality of a mixture (N_{mini})

   a) Acid + Acid OR Base + Base OR Neutral + Neutral

   $$N_{mix} = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

   If $V_1 = V_2$

   $$N_{mix} = \frac{N_1 + N_2}{2}$$

b)   Acid + Base

$$N_{mix} = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$$

If $V_1 = V_2$

$$N_{mix} = \frac{N_1 - N_2}{2}$$

13.   Relation connecting n-factor, M & N

$n_1 M_1 V_1 = n_2 M_2 V_2$ ...(1)

Since n represents n-factor

nM = N

$\therefore$ (1) becomes

$N_1 V_1 = N_2 V_2$

14.   Primary Standards

The solutes can be directly converted into a standard solution, whose concentration is known as called 1^0 standards.

eg : NaCl, Na_2CO_3, $H_2C_2O_4$. $2H_2O$ (oxalic acid) etc.

15.   Secondary Standards

The solutes cannot converted into a standard solution directly are called 2° standards because of their deliquescent and hydroscopic nature.

eg : NaOH, H_2SO_4, $KMnO_4$ etc.

To determine the concentration of unknown solution, a method known as titration is applied.

LIQUID SOLUTIONS

Solubility

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature.

Solubility depends upon

1)   Nature of solute   }   "Like dissolves Like"
2)   Nature of solvent   }   ie polar solutes dissolved
3)   Temperature   in polar solvents &
4)   Pressure   non – polar solutes dissolved
                             in non polar solvents

a)   **Solubility of a solid in a liquid**

When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution.

Some solute particles in solution collide with solid solute particles and get separated out of solution. This process is known as crystallisation.

An equilibrium is reached when the two processes occurs at the same rate.

Solute + Solvent $\rightleftharpoons$ Solution

At this stage, the concentration of solute is solution will remain constant under the given conditions. Such a solution in which no more solute can be dissolved at the same temperature and pressure (for gases as solutes) is called a saturated solution.

An unsaturated solution is the one in which more solute can be dissolved at the same temperature.

Concentration of solute in saturated solution in its solubility.

Effect of Temperature

Consider the equilibrium

Solute + Solvent $\rightleftharpoons$ Solution

This being a dynamic equilibrium, must follow Le Chattler's principle.

Effect of temperature on the solubility of a solid in a liquid can be explained by the equation.

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \Rightarrow \text{Van't Hoff's Equation}$$

K = Equilibrium constant

ΔH = Enthalpy change

a)   If in a nearly saturated solution, the dissolution process is endothermic ie., $\Delta H > 0$

$\log \dfrac{K_2}{K_1} > 0$ Since $T_2 > T_1$

ie $\dfrac{K_2}{K_1} > 1$

or $K_2 > K_1$

$\therefore$ As T $\uparrow$ equilibrium constant K$\uparrow$ ie., dissolution also increases.

b)   If the dissolution process is exothermic ie., $\Delta H < 0$

$\log \dfrac{K_2}{K_1} < 0$ since $T_2 > T_1$ & $\Delta H = -\text{ve}$

$\log \dfrac{K_2}{K_1} < 1$

or $K_2 < K_1$

$\therefore$ As T$\uparrow$ equilibrium constant K $\downarrow$ ie., dissolution decreases.

ii)   **Effect of Pressure**

Pressure does not have any significant effect on the solubility of solids in liquids. It is so because solids and liquids are highly incompressible.

b)   **Solubility of a gas in a liquid**

i)   Effect of pressure - Henry's Law

"The partial pressure of the gas in vapour phase (P) is proportional to the mole fraction of the gas (χ) in the solution".

$$P_{gas} \, \alpha \, \chi_{gas}$$

or

$$P_{gas} = K_{H_{gas}} \cdot \chi_{gas}$$

K_H is known as Henry's law constant which is a function of the nature of gas and temperature.

1)   At same temperature, different gases show different K_H values

eg : $K_H (N_2)$ = 76.48 kbar and $K_H(O_2)$ = 34.86 kbar at the same temperature of 298 K

2)   At different temperatures, same gas exhibit different K_H values.

eg : $K_H(N_2)$ = 76.48 kbar @ 293 K but 88.48 kbar @ 303 K.

Plot of P Vs χ
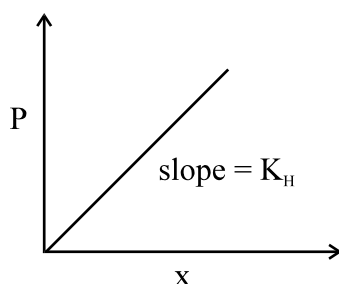
Since $K_H = \dfrac{P}{\chi}$, as $\chi \uparrow K_H \downarrow$ ie., a gas with low K_H has more solubility at the given conditions.

eg : HCHO (K_H at 298 K = 1.83 × 10^{-5}) has more solubility in water than He (K_H at 293 K = 144.97) in water.

ii)   **Effect of Temperature**

Since the dissolution of a gas in a liquid is same as that of condensation process (exo), as temperature increases dissolution (χ) decreases always.

$\therefore$ The solubility of a gas increases with decrease of temperature. This is whey aquatic species are more comfortable in cold water rather than warm waters.

NOTE

Henry's law also takes the form

$$\chi_{gas} = K_{H_{gas}} \cdot P_{gas}$$

$$\text{unit of } K_H = \text{unit of (pressure)}^{-1}$$

Application of Henry's Law

1)   In soft drink and soda water industry - to increase the solubility of CO_2 in soft drinks and soda water, the bottle is seated under high pressure.

2)   SCUBA (Self Contained Underwater Breathing Apparatus) divers experience high concentration of dissolved gases while breathing air at high pressure under water. When the divers came towards the surface, the pressure gradually decreases. This releases dissolved gases and lead to the formation of bubbles of N_2 in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life.

To avoid bends, the toxic effect of high concentration of N_2 in the blood the tanks used by scuba divers are filled with air diluted with He.

In the cylinder ;

N_2 > O_2 > He
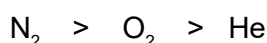
56.2% 32.1%   11.7%

3)   At high altitude, the partial pressure of O_2 is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitude or climbers. Low blood oxygen causes anoxia.

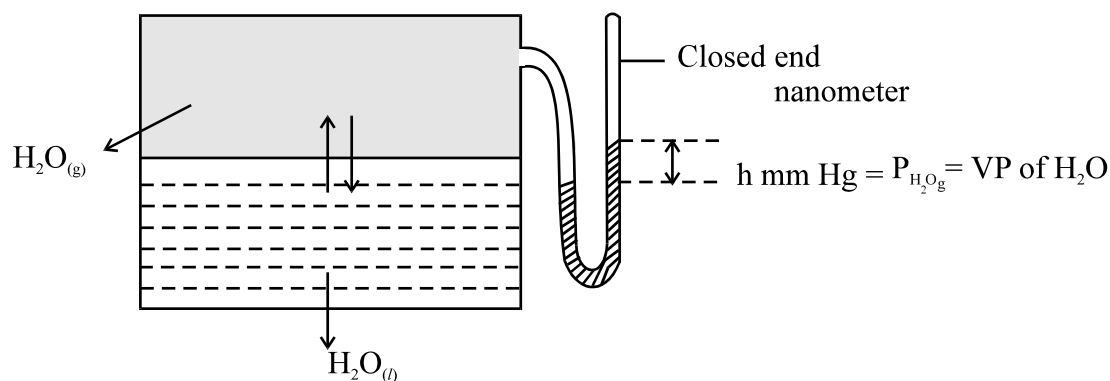**Limitations of Henry's Law**

Henry's law is not valid if

1)   the temperature is too low

2)   the pressure is very high

3)   gases reacts with solvent
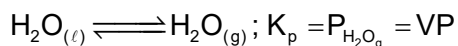
4)   gases undergo dissolution or association in solvent

eg : $NH_3 + H_2O \longrightarrow NH_4OH \longrightarrow NH_4^+ + OH^-$

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$
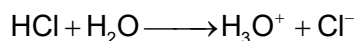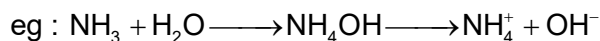
Liquid - Liquid Solutions

Vapour Pressure (VP)

VP of a liquid or a solution is the equilibrium pressure exerted by the vapours of a liquid or a solution at a particular temperature.

$H_2O_{(g)}$

$H_2O_{(l)}$

Closed end nanometer

h mm Hg $= P_{H_2O_g} =$ VP of H_2O

At equilibrium

$$H_2O_{(\ell)} \rightleftharpoons H_2O_{(g)} \; ; \; K_p = P_{H_2O_g} = VP$$

Since VP is the equilibrium constant in terms of pressure, VP changes with temperature only. Therefore while reporting VP of a liquid or a solution we should report the temperature always.

Effect of Temperature on Vapour Pressure

$$\log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \Rightarrow \text{Clausius} - \text{Clapeyron Equation}$$

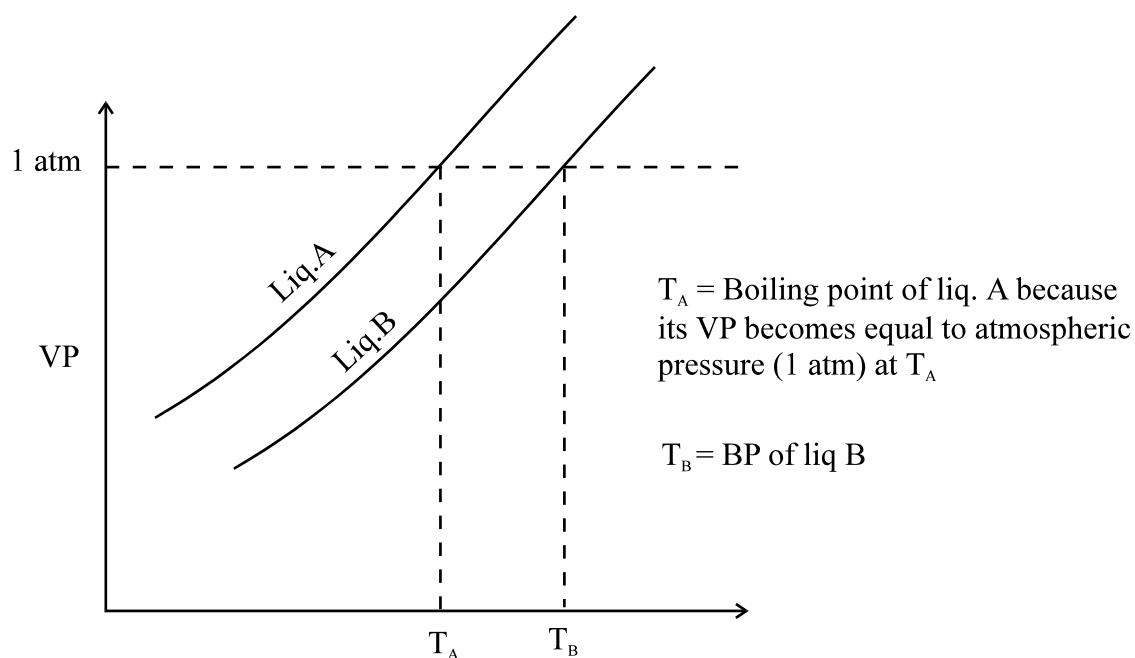Since evaporation is endothermic, $\Delta H > 0 (+ve)$. As temperature increases from T_1 to T_2 ($T_2 > T_1$).

$$\log\left(\frac{P_2}{P_1}\right) > 0$$

$$\frac{P_2}{P_1} > 1$$

$$P_2 > P_1$$

ie., VP ↑ with ↑ in T

VP Vs T graph

T_A = Boiling point of liq. A because its VP becomes equal to atmospheric pressure (1 atm) at T_A

T_B = BP of liq B

More volatile liquid A has low B.P & vice versa.

Vapour Pressure of Liquid - Liquid Solutions

Raoult's Law (Francois Marte Raoult)

"For a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution".

For component 1

$P_1 \alpha \chi_1$ and

For component 2

$P_2 \alpha \chi_2$

or $P_1 = P_1^0 \chi_1$ and $P_2 = P_2^0 \chi_2$

Here P_1^0 and P_2^0 are the respective V.P of pure components 1 and 2.

P_1 and P_2 are the respective V.P of components 1 and 2 in solution.

According to Dalton's Law of Partial Pressures,

Total V.pressure,

$P_T = P_1 + P_2$

ie., $\boxed{P_T = P_1^0 \chi_1 + P_2^0 \chi_2}$

$= P_1^0 (1 - \chi_2) + P_2^0 \chi_2 = P_1^0 + (P_2^0 - P_1^0) \chi_2$

ie.,

a)   Total vapour pressure over the solution can be related to the mole fraction of any one component.

b)   Total vapour pressure over the solution varies linearly with the mole fraction of component 2.

c)   Depending on the vapour pressures of the pure components 1 and 2, total V.P over the solution decreases or increases with the increase of the mole fraction of component 1.

Plot of VP Vs χ

$P_1 = P_1^0 \chi_1$ & $P_2 = P_2^0 \chi_2$

$y = mx$ $y = mx$
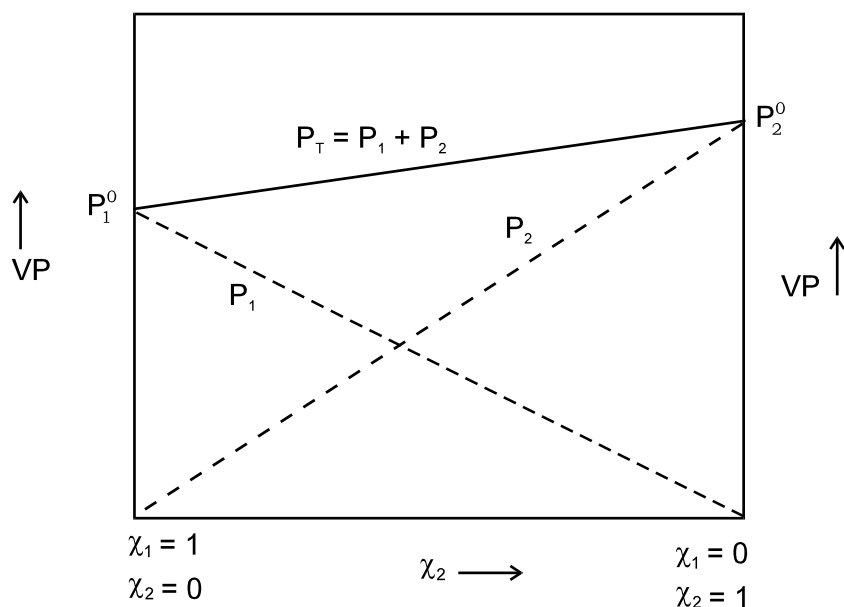
Here component 1 is less volatile than the component 2. ie., $P_1^0 < P_2^0$.

Composition of a Solution

A)   In solution phase ;

       Composition = χ_1 & χ_2

B)   In vapour phase

       Composition = Y_1 & Y_2

       According to Dalton's law of partial pressure,
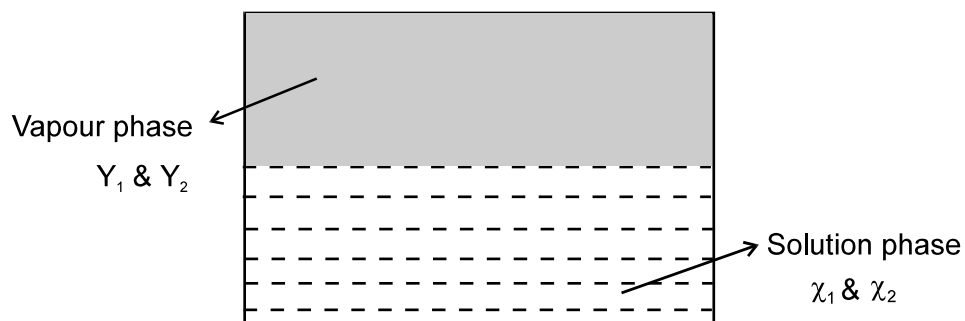
          $P_1^0 = P_T \cdot Y_i$

    or $Y_i = \dfrac{P_i}{P_T}$

       For binary solution,

$$Y_1 = \frac{P_1}{P_T} \quad \& \quad Y_2 = \frac{P_2}{P_T}$$

    or $Y_1 = \dfrac{P_1^0 \chi_1}{P_T} \quad \& \quad Y_2 = \dfrac{P_2^0 \chi_2}{P_T}$

Vapour phase
Y_1 & Y_2

Solution phase
χ_1 & χ_2

Verification of relation between X & Y

$$Y_1 = \frac{P_1}{P_{Total}} = \frac{P_i\,\chi_1}{P_T}$$

or $\qquad Y_1 = \dfrac{P_1^0\,\chi_1}{P_1^0\chi_1 + P_2^0\chi_2}$

or $\qquad \dfrac{1}{Y_1} = \dfrac{P_1^0\,\chi_1 + P_2^0\chi_2}{P_1^0\chi_1} = 1 + \dfrac{P_2^0\chi_2}{P_1^0\chi_1}$
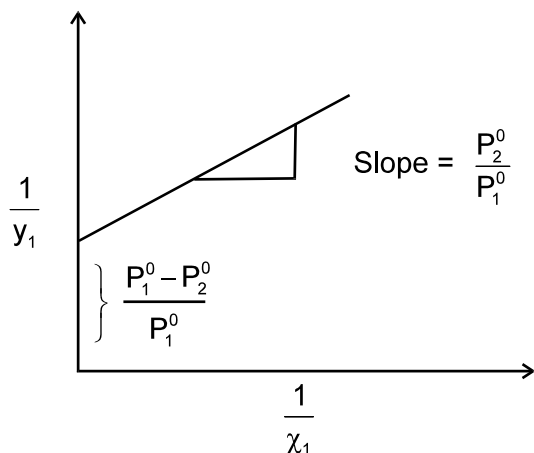
$$\frac{1}{Y_1} = 1 + \frac{P_2^0\,(1-\chi_1)}{P_1^0\chi_1} \;\; (\chi_2 = 1-\chi_1) = 1 + \frac{P_2^0 - P_2^0\chi_1}{P_1^0\chi_1}$$

$$= 1 + \frac{P_2^0}{P_1^0} + \frac{P_2^0}{P_1^0\,\chi_1} = 1 - \frac{P_2^0}{P_1^0} + \frac{P_2^0}{P_1^0\,\chi_1}$$

ie., $\qquad \dfrac{1}{Y_1} = \left(\dfrac{P_1^0 - P_2^0}{P_1^0}\right) + \dfrac{P_2^0}{P_1^0} \times \dfrac{1}{\chi_1}$

$\dfrac{1}{Y_1}$ Vs $\dfrac{1}{\chi_1}$ graph

$$\underset{y}{\frac{1}{Y_1}} = \underset{c}{\left(\frac{P_1^0 - P_2^0}{P_1^0}\right)} + \underset{m}{\left(\frac{P_2^0}{P_1^0}\right)} \underset{x}{\frac{1}{\chi_1}}$$

$$\text{Slope} = \frac{P_2^0}{P_1^0}$$

$$\frac{P_1^0 - P_2^0}{P_1^0}$$

Raoult's Law as a special case of Henry's Law

According to Raoult's Law

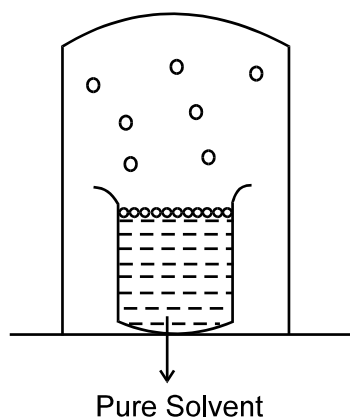$$P_1^0 = P_1^0 \, \chi_1^0 \qquad \qquad ...(1)$$

According to Henry's Law

$$P_1^0 = K_{H_i} \, \chi_1^0 \qquad \qquad ...(2)$$

$\therefore$ Raoult's law is a special case of Henry's law in which $KH_i = P_i^0$

Vapour Pressure of Solution of Solids in Liquids - Raoult's law in General Form

In pure liquids, the entire surface is occupied by the molecules of liquid.

Pure Solvent

If a **non-volatile solute** is added to a solvent to give a solution, the V.P of the solution is solely from solvent alone.

$\therefore P_S = P_1 + P_2 = P_1$ only because 2 is non volatile.

In the solution, the surface has both solute and solvent molecules, thereby the fraction of the surface covered by the solvent molecules get reduced. Consequently, the number of solvent molecules escaping from the surface is corresponding reduced, thus the V.P is also reduced.

Solute molecule
Solvent molecule
Solution
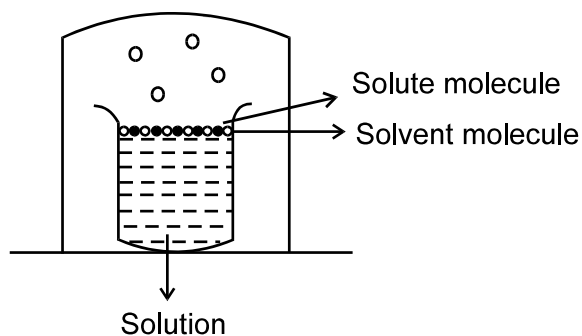
The decrease in the V.P of solvent depends on the quantity of non-volatile solute present in the solution irrespective of its nature.

ie., $P_1 < P_1^0$

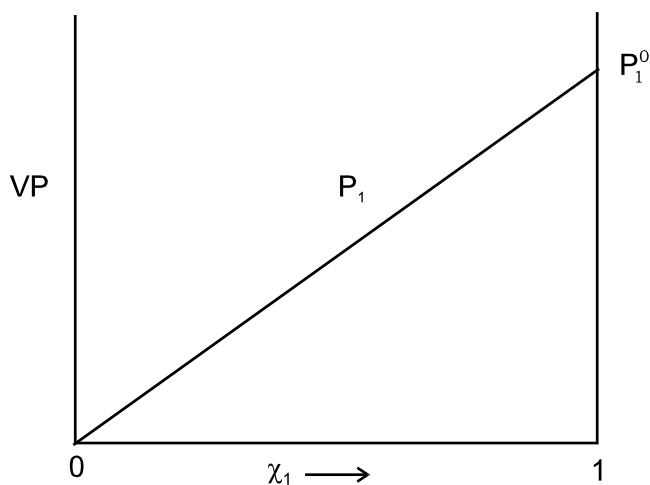$\therefore$ Lowering of $VP = \Delta P_1 = P_1^0 - P_1$

$\therefore$ Raoult's law in general form can be stated as : "For any solution the partial VP of each volatile component in the solution is directly proportional to its mole fraction".

$\therefore$ If the solute is non-volatile,

$P_1 \, \alpha \, \chi_1$ only

ie., $P_1 = P_1^0 \chi_1$

P_1 Vs χ_1 Graph

Types of Solutions Based on Raoult's Law

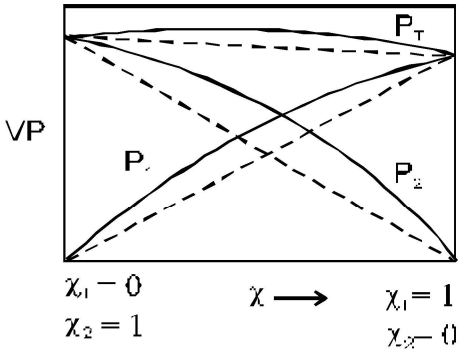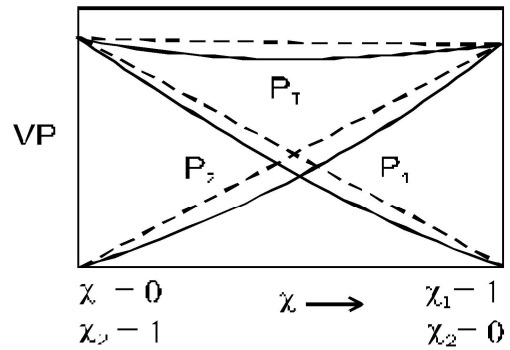Based on Raoult's law solutions are classified into 2 types.

1. **Ideal Solutions**

    •   The solutions which obeys Raoult's law over the entire range of concentration are called ideal solutions.

    •   Two properties are

        a)   Enthalpy of mixing $\Delta_{mix}H=0$

        b)   Volume of mixing $\Delta_{mix}V=0$.

    •   At molecular level, the intermolecular attractive interactions will be of two types A-A and B-B, whereas in solution, A-B interaction also be present. But A-B has same strength as that of A-A and B-B interactions.

    •   Perfect ideal solutions are very rare but some solutions are nearly ideal.

        egs : 1) n-hexane + n-heptane

                 2) Bromoethane + Chloroethane

                 3) Benzene + Toluene

                 4) Chlorobenzene + Bromobenzene etc.

2. **Non-Ideal Solutions**

    •   When a solution does not obey Raoult's law over the entire range of concentrations, then it is called a non-ideal solution.

    •   Two main properties are

        a) $\Delta_{mix}H\neq0$

        b) $\Delta_{mix}V\neq0$

Type of Non-Ideal Solutions

	Non ideal solutions with +ve deviation		Non ideal solutions with -ve deviation
1)	VP is higher than that predicted by Raoult's law	1)	VP is lower than that predicted by Raoult's law
2)	$\Delta V_{mix} > 0$, $\Delta H_{mix} > 0$ ⟹ +ve, Cold Solution	2)	$\Delta V_{mix} < 0$, $\Delta H_{mix} < 0$ ⟹ −ve, Warm Solution
3)	A-B interaction is weaker than A-A and B-B interaction and A and B will easily escaped into gaseous phase	3)	A-B interaction is stronger than A-A and B-B interaction and the escaping tendency into vapour phase for A and B decreases
4)	VP Vs χ graph ;	4)	VP Vs χ graph ;
5)	Examples : a) Ethanol + water b) Acetone + CO_2 c) Methanol + water d) Acetone + benzene e) Toluene + CCl_4	5)	Examples : a) HNO_3 + water b) HCl + water c) Acetone + Chloroform d) Phenol + Aniline e) Acetic acid + Pyridine

NOTE - Explanation for Examples

1. **Acetone + Chloroform**
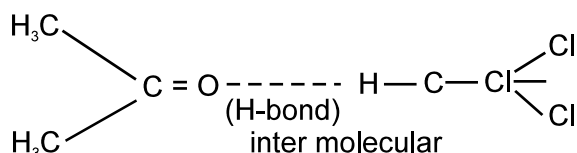
Here the acetone - chloroform interaction is stronger than acetone-acetone as well as chloroform-chloroform interactions. Therefore, this solution exhibit -ve deviation from ideal behaviour because the strong interaction decreases the escaping tendency of two liquids which decreases the VP of solution.

2. **Ethanol + Water**

Here ethanol - ethanol and water - water interaction is already strong because it is a H-bond. Compared to the individual H-bonding, the H-bonds formed between ethanol and water is not so strong which increases the escaping tendency of these two liquids results in +ve deviation from ideal behaviour.

For solution of any types whether it is ideal or non-ideal,

$$\Delta S_{mix} = + ve \,(\text{disorder increases})$$
$$\Delta G_{mix} = - ve \,(\text{dissolution is spontaneous})$$

Azeotropes

• These are the binary mixtures having the same composition in liquid and vapour phase and boils at a constant temperature.

• It is not possible to separate the components by fractional distillation.

• Azeotropes are formed by solutions which does not obey Raoults law ie., non-ideal solutions.

• Azeotropes are classified into 2 types

   a) Minimum boiling azeotropes

   b) Maximum boiling azeotropes

	Minimum Boiling Azeotropes		**Maximum Boiling Azeotropes**
1)	Formed by non-ideal solutions having +ve deviation	1)	Formed by non-ideal solutions having -ve deviation
2)	They boils at a temperature lower than the boiling points of individual liquids (minimum boiling)	2)	They boils at a temperature higher than the boiling points of individual liquids (maximum boiling)
3)	Ethanol-water mixture - 95% by volume of ethanol forms azeotropes	3)	HNO_3 - water mixture - 68% by volume of HNO_3 forms azeotropes

Azeotropic Distillation

- Azeotropes cannot be repeated by fractional distillation due to constant boiling point.

- a)   By adding a suitable chemical we can separate one of the component thereby separation of components is possible.

  b)   By adding a third component called entrainers which decreases the VP of one of the component thereby boiling point may differ, then we can perform fractional distillation $\Rightarrow$ azeotropic distillation.

Colligative Properties (CP)

All the properties depend on the number of solute particles irrespective of this nature relative to the total number of particles present in the solution are called colligative properties.

(Co = together   ligare = to bind $\Rightarrow$ Latin words)

$$CP \; \alpha \; n_2 \;\; OR \;\; CP \; \alpha \; \frac{W_2}{M_2}$$

Major CP are

1) Relative lowering of VP (RLVP) - $\Delta P_1 / P_1^0$

2) Elevation of Boiling point - ΔTb

3) Depression of freezing point - ΔTf

4) Osmotic pressure - π

RLVP ($\Delta P_1 P_1^0$)

The VP of a solvent in solution (VP of solution in the case of a non-volatile solute) is less than that of pure solvent.

ie., $P_1 < P_1^0$

$\therefore$ Lowering of VP = $\Delta P_1 = P_1^0 - P_1$

According to Raoult's law, $P_1 = P_1^0 \chi_1$

$$\therefore \Delta P_1 = P_1^0 - P_1^0 \chi_1 = P_1^0 (1 - \chi_1) = P_1^0 \chi_2$$

$$\therefore RLVP = \frac{\Delta P_1}{P_1^0} = \frac{P_1^0 - P_1}{P_1^0} = \chi_2 = \frac{n_2}{n_1 + n_2}$$

For dilute solutions $n_2 << n_1$

$\therefore n_1 + n_2 \approx n_1 ;$

$$\therefore \quad \frac{P_1^{\;0} - P_1}{P_1^{\;0}} = \frac{n_2}{n_1}$$

Depends directly on n_2, hence it is colligative property

$$\therefore \frac{P_1^0 - P_s}{P_1^0} = \frac{n_2}{n_1} = \frac{w_2 M_1}{M_2 w_1} \qquad\qquad (P_s = P_1)$$

But for all cases, $\dfrac{P_1^0 - P_s}{P_1^0} = \dfrac{n_2}{n_1 + n_2}$

or $\dfrac{P_1^0}{P_1^0 - P_s} = \dfrac{n_1}{n_2} + 1$

ie., $\dfrac{P_1^0}{P_1^0 - P_s} - 1 = \dfrac{n_1}{n_2}$; $\dfrac{P_1^0 - P_1^0 + P_s}{P_1^0 - P_s} = \dfrac{n_1}{n_2}$

ie., $\dfrac{P_1}{P_1^0 - P_s} = \dfrac{n_1}{n_2}$

or $\dfrac{P_1 - P_s}{P_s} = \dfrac{n_2}{n_1}$
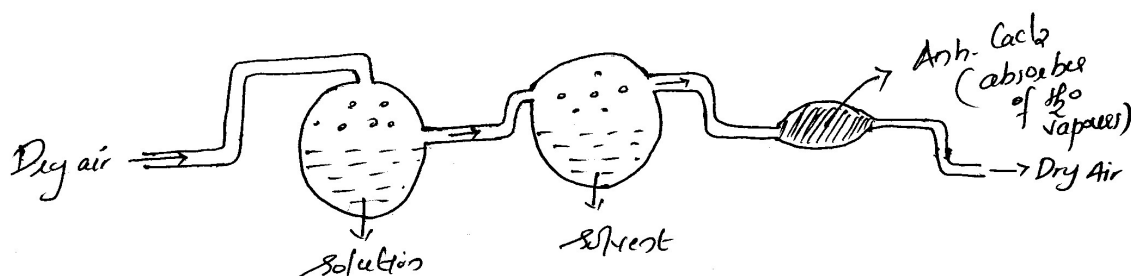
Calculation of M$_2$

For dilute solns,

$$\frac{P_1^0 - P_s}{P_1^0} = \frac{w_2 M_1}{w_1 M_2}$$

$$M_2 = \left(\frac{P_1^0}{P_1^0 - P_s} \right) \left(\frac{w_2 M_1}{w_1} \right)$$

Ostwald & Wacker Method

This method verifies experimentally the RLVP. The experimental set up is given as :

The solution chamber, solvent chamber and anh.CaCl$_2$ guard tube are previously weighed.

Here, weight loss in solution chamber $\alpha\, P_1$

weight loss in solvent chamber $\alpha\, P_1^0 - P_1$

$$\therefore \frac{\text{Weight loss in solvent chamber}}{\text{Total weight loss in both chamber}} = \frac{P_1^0 - P_s}{P_1^0}$$

Total weight gain in $CaCl_2$ tube ...(1)

We know that,

$$\frac{P_1^0 - P_s}{P_1^0} = \frac{w_2 M_1}{M_2 w_1} \qquad ...(2)$$

From (1) & (2)

$$\frac{\text{Weight loss in solvent chamber}}{\text{Total weight loss in both chamber}} = \frac{w_2 M_1}{M_2 w_1}$$

Total weight gain $CaCl_2$ tube

Hence RLVP is verified

Elevation of Boiling Point (ΔT_b)

- BP of a liquid or a solution is the temperature at which its VP becomes equal to atmospheric pressure.

- At 1 atm, BP is called normal BP

  Normal BP of H_2O = 100°C

  At 1 bar, BP is called standard BP

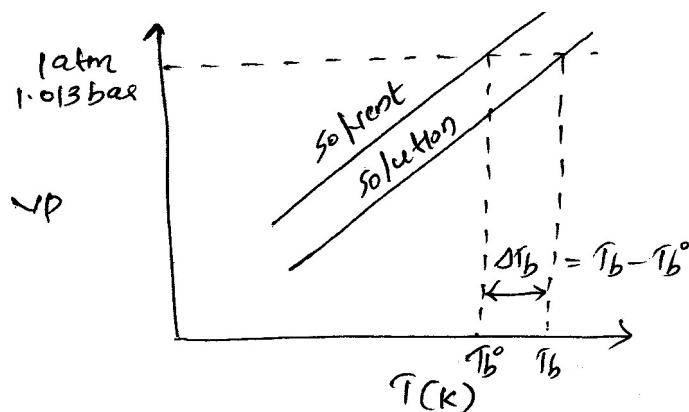 Standard BP of water = 99.6°C

  ie., 1 atm = 1.013 bar

- When a non-volatile solute is added to a volatile liquid the VP of the solvent in solution decreases. This decrease in VP increases the BP of solution and the increase in BP is known as elevation of BP is ΔT_b .

  If Tb° is the BP of pure solvent and T_b is the BP of solution,

  $T_b > T_b^0$

  $\therefore$ Elevation of BP $\Delta T_b = T_b - T_b^0$

VP Vs T curve

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From the graph,

$\Delta P_1 \, \alpha \, \Delta T_b$ ...(1)

From RLVP

$\Delta P_1 \, \alpha \, \chi_2$ ...(2)

$\therefore$ $\Delta T_b \, \alpha \, \chi_2$

$\Delta T_b = k \cdot \chi_2,$ where k = proportionality constant = $k \cdot \dfrac{n_2}{n_1 + n_2}$

For dilute solution, $n_1 + n_2 \approx n_1$

$\therefore \; \Delta T_b = k \cdot \dfrac{n_2}{n_1}$

Since ΔT_b proportional to n_2, number of moles of solute, then ΔT_b is a colligative property.

$\Delta T_b = \dfrac{k \cdot n_2 M_1}{w_1}$

Since k and M_1 are constant, $K \cdot M_1 =$ constant $= K_b$ known as molal elevation constant or elevation of BP constant or ebullioscopic constant.

$\therefore \; \Delta T_b = k_b \cdot \dfrac{n_2}{w_1} = k_b \cdot m,$ molality of solution

OR $\Delta T_b = \dfrac{k_b \cdot w_2 \cdot 1000}{M_2 \cdot w_1}$

OR $\Delta T_b = T_b - T_b^0 = k_b \cdot m = \dfrac{k_b \cdot w_2 \cdot 1000}{M_2 \cdot w_1}$

Experimental verification of $\Delta T_b = $ Lansberger method

Ebullioscopic Constant, K_b ;

K_b is a property of solvents.

$K_b = \dfrac{\Delta T_b}{m} = \dfrac{K}{kgmol^{-1}} = $ K kg mol^{-1} or K m^{-1}

For a molal solution,

$K_b = \Delta T_b$

$\therefore \; K_b$ is defined as the elevation of BP for a 1 molal solution.

K_b for H_2O = 0.52 K kg mol^{-1}

Calculation of M$_2$

$$M_2 = \frac{K_b.w_2.1000}{\Delta T_b.w_1}$$

Determination of K$_b$ for a solvent

$$K_b = \frac{R(T_b^\circ)^2}{1000\,\ell v}$$

R = Universal gas constant

T_b° = B.P of pure solvent

ℓ_v = latent heat of vapourisation for unit mass of solvent $= \Delta_V H / M_1$

$$\therefore K_b = \frac{RM_1\,(T_b^\circ)^2}{1000\Delta_v H} = \frac{\Delta_v H}{M_1}$$

$\Delta_V H$ = Molar heat of vapourisation

M_1 = Molar mass of solvent in g / mol

Depression of Freezing Point (ΔT_f)

- FP of a substance is defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its VP in solid phase. ie., at FP both liquid and solid form co exist.

- When a non-volatile solute is added to a solvent VP of solution decreases which decreases the FP of solution and the decrease is known as depression of FP (ΔT_f).

  If T_f° be the FP of pure solvent and T_f be that of solution, then

  $$T_f^\circ > T_f$$

  $$\therefore \text{ Depression of FP} = \Delta T_f = T_f^\circ - T_f$$

VP Vs T curve
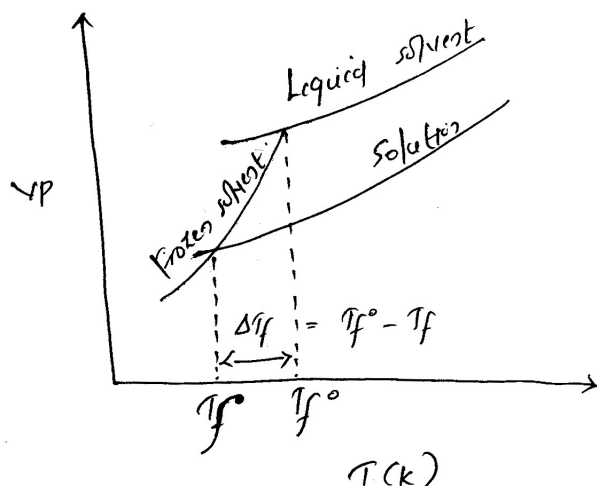
Similar to ΔT_b, we can show that

$$\Delta T_f = T_f^\circ - T_f = k_f.m = \frac{k_f.w_2.1000}{M_2.w_1}$$

The proportionality constant k_f is known as molal constant OR depression of FP constant OR cryoscopic constant.

K_f is a property of solvent.

$$K_f = \frac{\Delta T_f}{m} = K\,kg\,mol^{-1}$$

For a 1 molal solution, $k_f = \Delta T_f$ $\therefore$ K_f is defined as depression of FP for a 1 molal solution.

K_f of water $= 1.86\,K\,kg\,mol^{-1}$

Calculation of M$_2$

$$M_2 = \frac{K_f . w_2 . 1000}{\Delta T_f . w_1}$$

Determination of K$_f$

$$\ell_f = \text{latent heat of fusion}$$

$$K_b = \frac{R(T_f^o)^2}{1000\,\ell_f} \qquad = \frac{\Delta_f H}{M_1}$$

$$\Delta_f H = \text{Molar heat of fusion}$$

$$\therefore\ K_f = \frac{RM_1\,(T_f^o)^2}{1000\Delta_v H}$$

Experimental verification of $\Delta T_f = $ Beckmann Method

Note :

- **Rast Method**

  In Rast Method, the solvent used is camphor with a high K_f value of 40 K kg mol^{-1}. By using this solvent, ΔT_f is obtained as a measurable value.

- Antifreeze solutions and use of NaCl & CaCl$_2$ to remove ice from the roads are application of ΔT_f .

4. **Osmotic Pressure (π)**

    Osmosis

    The flow of solvent from its higher concentration into lower concentration OR from dilute solution into concentrated solution through a semi permeable membrane (SPM) is known as osmosis.

    eg :   1)   Raw mangoes sheivel when pickled in brine

            2)   Wilted flowers revive when placed in fresh water

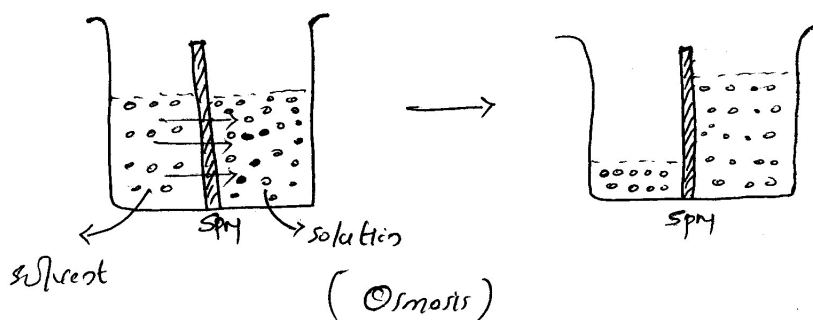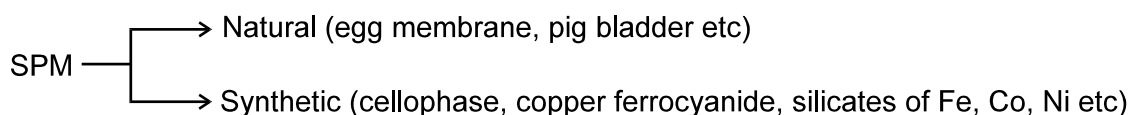   3)   Blood cells collapse when suspended in salini solution

            4)   Carrot become limb because of wake loss in atmosphere and can become firm when placed in water

            5)   Water movement from soil into plant roots and subsequently into upper portions of the plant.

6) Preservation of meat by salting and of fruits by adding sugar protects against bacterial action because bacterium on salted meat or candid fruit loses water sheivels and dies.

7) People taking of lot of salt or salty food experience water retention in tissue cells and intercellular spaces. This results puffiness or swelling called **Edema**.
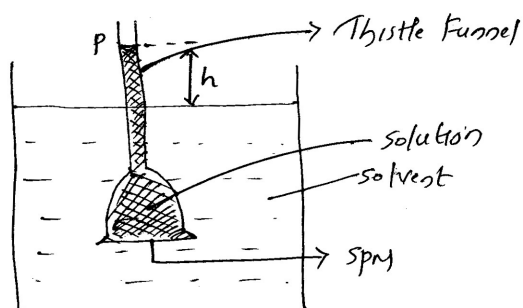
Semi-Permeable membranes (SPM)

SPM allows the passage of solvent molecules only.

SPM $\longrightarrow$
- $\longrightarrow$ Natural (egg membrane, pig bladder etc)
- $\longrightarrow$ Synthetic (cellophase, copper ferrocyanide, silicates of Fe, Co, Ni etc)

Osmotic Pressure (π)

The minimum pressure that just stops the flow of solvent is called osmotic pressure (π) solution.

h = Osmotic rise

We know that $\pi = h\rho g$; ρ = density of solution

$g = 9.8 \text{ ms}^{-2}$

Experimentally it was found that

$\pi \, \alpha \, C$ and $\pi \, \alpha \, T$

ie., $\pi \, \alpha \, CT$

$\pi = CRT$ R = Gas constant

C = Concentration in terms of molarity

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or $\pi = \dfrac{n_2 RT}{V}$

Since $\pi \, \alpha \, n_2$, π is a colligative property

$$\pi = \dfrac{w_2 RT}{M_2 V}$$

Calculation of M$_2$

$$M_2 = \dfrac{w_2 RT}{\pi V}$$

Advantages of Osmotic Pressure Measurement

1. This method is widely used for determine molar masses of proteins, polymers and other macromolecules and the values are more accurate and large because this method is carried out at room temperature. Otherwise, biomolecules becomes unstable at elevated and depressed temperatures and polymers have poor solubility.

2. Taking molarity instead of molality

Isotonic solutions

Two solutions having same osmotic pressure a given temperature are called isotonic solutions.

When isotonic solutions are separated by SPM no osmotic occurs between them.

eg : π associated with fluid inside the blood cells is equivalent to that of 0.9% (w/v) NaCl solution.

$\therefore$ RBC and 0.9% w/v NaCl (normal saline) are isotonic $\therefore$ IV injection (Intravenous injection) uses 0.9% w/v normal saline solution.

For isotonic solutions,

$\pi_1 = \pi_2$

$C_1 RT = C_2 RT$

ie., $C_1 = C_2$

$\dfrac{n_1}{v} = \dfrac{n_2}{v}$

If volume is same, $n_1 = n_2$

$\dfrac{w_1}{M_1} = \dfrac{w_2}{M_2}$

Hypertonic & Hypotonic Solutions

If two solutions have different osmotic pressure or different concentrations,

a) the one with high concentration is called hypertonic

b) the one with low concentration is called hypotonic

Reverse Osmosis (RO)

The direction of osmosis can be reversed if a pressure larger than the osmotic is applied to the solution side. That is, pure solvent flows out of the solution side. That is, pure solvent flows out of the solution through SPM. This phenomenon is called RO.

RO is the main principle behind desalination of sea water
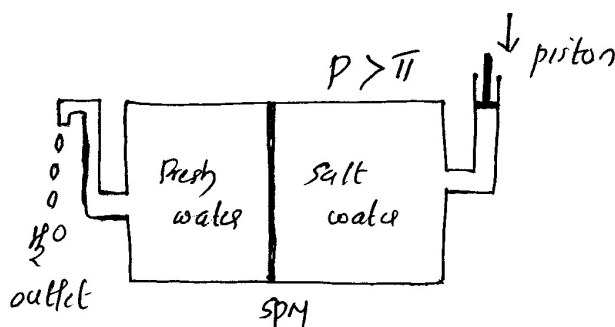
Usually SPM in desalination of sea water is a film of cellulose acetate.

Experimental verification of osmotic pressure is known as

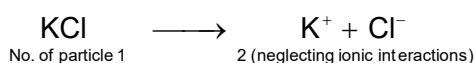1)   Harteley & Berkely Method

2)   Morse & Frazer Method

Abnormal Molar Masses

The molar mass of solute obtained from colligative properties ie., apparent molecular mass has a magnitude that is either lower or higher than the expected or normal values. This abnormalities is known as abnormal molar masses.

This abnormal molar masses is due to the association or dissociation of solutes in solvent.

i.   **Dissociation**

Consider dissociation of KCl in water

$$\underset{\text{No. of particle 1}}{\text{KCl}} \longrightarrow \underset{\text{2 (neglecting ionic interactions)}}{K^+ + Cl^-}$$

Normal molar mass of KCl = 74.5 g

Abnormal (apparent OR observed)

molar mass of KCl = 37.25 g

As number of particles doubles, CP also doubles and molar mass become half because

$$CP \, \alpha \, n_2$$

OR $CP \, \alpha \, \dfrac{1}{M_2}$

ii.   **Association**

Consider the association (Dimerisation) of acetic acid in benzene

$$\underset{\text{No.of particles}}{\underset{2}{2CH_3COOH}} \rightleftharpoons \underset{1}{(CH_3COOH)_2}$$
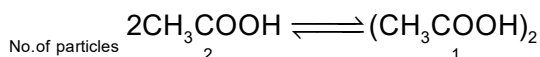
Normal molar mass of CH_3COOH = 60 g

Abnormal molar mass of CH_3COOH = 120 g

As the number of particles halved, CP also halved and molar mass become doubles because

$$CP \alpha \, n_2$$

OR $CP \, \alpha \, \dfrac{1}{M_2}$

These abnormalities in molar mass of solute due to association or dissociation is known as abnormal molar masses.

van't Hoff's Factor (i)

In order to account for abnormal molar masses of solute, van't Hoff's factor (i) is introduced by J.H. van't Hoff

i is defined as

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}} = \frac{\text{Observed Colligative Properties}}{\text{Calculated Colligative Property}}$$

$$= \frac{\text{Total no. of moles of particles after association}}{\text{No. of moles of particles before asso / disso}}$$
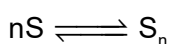
- Assuming 100% dissociation of solutes,

  i for NaCl, KCl etc = 2

  i for K_2SO_4, Na_2SO_4 etc = 3

  i for $K_4[Fe(CN)_6]$ = 5

  For non-electrolytes such as glucose, sucrose, urea, alcohols etc i = 1

- Association of solute in solvent is represented as

  $$nS \rightleftharpoons S_n$$

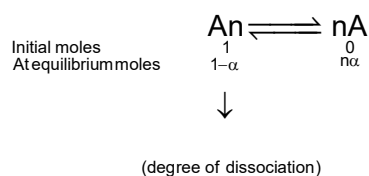 100% Dimerisation   i = 1/2

  100% Termerisation   i = 1/3 etc

  $\therefore$ 100% association   i = 1/n

A. **Dissociation**

  - i > i

  - A general dissociation of solute is represented as

  $$\underset{\substack{\text{Initial moles} \quad \ \ 1 \qquad \ \ 0 \\ \text{At equilibrium moles} \ \ 1-\alpha \quad n\alpha}}{An \rightleftharpoons nA}$$

  $\downarrow$

  (degree of dissociation)

Total number of moles $n_T = 1 - \alpha - n\alpha = 1 + (n-1)\alpha$

van't Hoff factor $\quad i = \dfrac{n_T}{n_i} = i = \dfrac{1 + (n-1)\alpha}{1}$

ie., $\quad \alpha = \dfrac{i-1}{n-1}$

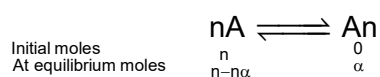● **Dissociation constant (K_d)**

$K_d = \dfrac{C\alpha^2}{1-\alpha}$

C = Concentration

$\alpha = $ Degree of dissociation

B. **Association**

- ● i < 1

- ● A general association of solute is represented as

$$nA \rightleftharpoons An$$

Initial moles $\quad$ n $\quad$ 0
At equilibrium moles $\quad$ n$-$nα $\quad$ α

$n_T = n - n\alpha + \alpha$

$i = \dfrac{n_T}{n_i} = \dfrac{n - n\alpha + \alpha}{n} = 1 - \alpha + \dfrac{\alpha}{n} \; ; \; i = 1 + \left(\dfrac{1}{n} - 1\right)\alpha$

ie., $\quad \alpha = \dfrac{i-1}{\dfrac{1}{n} - 1} \quad$ or $\quad \alpha = \dfrac{1-i}{1 - 1/n}$

● **Association Constant (K_a)**

$K_a = \dfrac{C\alpha^2}{1-\alpha}$

In general, the abnormalities of molar mass can be minimized by multiplying n_2 with i. Therefore modified CPs are

1) RLVP $\quad\quad \dfrac{P_1^0 - P_s}{P_1^0} = \dfrac{in_2}{n_1 + in_2}$

2) $\Delta T_b \quad\quad\quad \Delta T_b = ik_b.m$

3) $\Delta T_f \quad\quad\quad \Delta T_f = ik_f.m$

4) $\pi \quad\quad\quad\quad \pi = iCRT$

Variation of CP with i

1) $\dfrac{P_1^0 - P_s}{P_1^0} = i\chi_2$; $P_s = P_1^0 - i\chi_2 P_1^0$

   $A_s\ i\uparrow P_s\downarrow$

2) $\Delta T_b = ik_b m$; $T_b = T_b^0 + ik_b m$

   $A_s\ i\uparrow T_b\downarrow$

3) $\Delta T_f = ik_f m$; $T_f^0 - T_f\ ik_f m$; $T_f = T_f^0 - ik_f m$

   $A_s\ i\uparrow T_f\downarrow$

4) $\pi = iCRT$

   $\pi\ \alpha\ i$

   $A_s\ i\uparrow \pi\downarrow$

$\therefore$ VP of solution (P_s) & Freezing point of solution (T_f) $\alpha\ \dfrac{1}{i}$

   Osmotic pressure (π) & Boiling point of solution (T_b) $\alpha\ i$

Isotonic Solutions & van't Hoff's Factor

   For isotonic solutions

$\pi_1 = \pi_2$

$i_1 C_1 RT = i_2 C_2 RT$; $i_1 C_1 = i_2 C_2$

$i_1 \dfrac{n_1}{V} = i_2 \dfrac{n_2}{V}$ (Assume that volume of two solutions are equal)

ie., $i_1 \dfrac{w_1}{M_1} = i_2 \dfrac{w_2}{M_2}$