→ Solutions:→

- Solution is a homogeneous mixture of two or more substances having uniform properties (such as density, refractive index, etc.) throughout.

Example:- If sugar lump is dipped in a beaker of water, the lump disintegrates and within a short time disappears into the liquid phase. In this process, the molecules of sugar leave the crystal structure of solid and become uniformly dispersed throughout the water.

→ Components:→

- The substances making up a solution are called components of the solution.

Example:- The solution of sugar in water is an example of a two component system containing one liquid phase.

→ Solute and solvent :→

- The component having the same physical state as the solution is termed as solvent, and the other component solute. Thus, in the solution of sugar in water. water is solvent whereas solute is sugar.

There is no theoritical distinction between the terms solvent and solute, since the molecules of both are uniformly distributed throughout the solution.

Example:- A solution made by mixing equal volumes of ethyl alcohol and water. Either may, with equal justification, be considered to be dissolved in each other.

However, the component present in larger amount is called solvent whereas the component present in smaller amount is called the solute.

→ Types of solutions:→

- Since there are three states of matter, there are theoritically nine possible classes or types of solutions:-

S. No.	Solute	Solvent	Type of the solution	Examples
1.	Gas	Gas	Gas-Gas	Any mixture of gases as in air
2.	Gas	Liquid	Gas-liquid	Carbon dioxide in aerated bottles ; mineral water
3.	Gas	Solid	Gas-Solid	Hydrogen adsorbed on palladium
4.	Liquid	Gas	Liquid-Gas	Moisture in air when we have mist
5.	Liquid	Liquid	Liquid-Liquid	Alcohol in water, benzene in toluene
6.	Liquid	Solid	Liquid-Solid	Hg in gold
7.	Solid	Gas	Solid-Gas	Camphor in air, iodine vapour in air
8.	Solid	Liquid	Solid-Liquid	sugar in water, common salt in water
9.	Solid	Solid	Solid solutions	Alloys like brass containing zinc in copper.

→ Methods of expressing concentrations of solutions:→

1. Molarity (M):→

- Molarity is defined as number of moles of solute present in one litre of the solution.

$$M = \frac{\text{Moles of solute}}{\text{Volume of solution}} = \frac{n_A}{V\,(\text{in litre})}$$

Example:- A 0.1M solution of NaCl means that one litre of such a solution contains 0.1 mole of NaCl.

2. Molality (m):→

- Molality is defined as number of moles of solute present in one kilogram of the solvent.

$$m = \frac{\text{Moles of solute}}{\text{Mass of solvent}} = \frac{n_A}{\text{Kg of solvent}}$$

Example:- A 1m solution of cane sugar contains 1 mole of cane sugar in 1 kg of water.

✱ In laboratory, molarity is generally used to express concentrations of solutions. But the main drawback of this mode is that its value depends upon temperature due to expansion or contraction of the liquid.

The main advantage of molality over molarity is that molality does not depends upon temperature.

3. Normality(N):→

- Normality is defined as number of gram equivalents present in one litre of the solution.

$$\boxed{N = \frac{\text{No. of gm eq. of solute}}{\text{Volume of solution}} = \frac{n_B}{V\,(\text{in litre})}}$$

Example:- A 0.1N $AgNO_3$ solution means that it contains 0.1 gm equivalent of $AgNO_3$ per liter of the solution.

4. Mole fraction:→

- It is the ratio of moles of one component to the total number of moles of component (solute as well as solvent) of the solution.

$$\boxed{\text{Mole fraction of a component} = \frac{\text{Moles of a componet}}{\text{Total number of moles of component of the solution}}}$$

Example:- Suppose, a solution is prepared from n_A moles of A and n_B moles of a B in a fixed quantity of the solution. Then

$$\boxed{\text{mole fraction of A} = \frac{\text{Moles of A}}{\text{Moles of A + Moles of B}}}$$

or

$$\boxed{x_A = \frac{n_A}{n_A + n_B}}$$

$$\boxed{\text{mole fraction of B} = \frac{\text{Moles of B}}{\text{Moles of A + Moles of B}}}$$

or

$$\boxed{x_B = \frac{n_B}{n_A + n_B}}$$

- The sum of the mole fraction of the components of a mixture (or a solution) is unity. Then

$$\boxed{\sum x_i = 1}$$

→ The less frequently used concentration units are :-

1 Mass percent :→

- The mass percent of a component A in solution is defined as

$$\text{Mass \% A} = \frac{\text{Mass of A}}{\text{Total mass}} \times 100$$

2. Mole percent :→

- The mole percent of a component A in solution is defined as

$$\text{Mole \% A} = \frac{\text{Mole of A}}{\text{Total moles}} \times 100$$

3. Parts per million (ppm) :→

- The concentration of a component A in solution in ppm is defined as

$$(\text{ppm})_A = \frac{\text{Mass of A}}{\text{Total mass}} \times 10^6$$

✿ In a two-component (binary) solution, it is customary to denote the solvent by subscript 1 and solute by subscript 2.

4. Mass fraction:→

- The mass fraction of a component in a solution is expressed as the mass of that component per unit mass of solution.

Suppose w_A and w_B are the masses of components A and B respectively. Then

$$\text{Mass fraction of A} = \frac{w_A}{w_A + w_B}$$

$$\text{Mass fraction of B} = \frac{w_B}{w_A + w_B}$$

→ Vapour pressure of liquid:→

- Suppose a pure liquid is placed in a beaker which is covered with a bell jar. A small fraction of molecules of liquid will always possess sufficient minimum energy so that they may escape from the liquid in the form of vapours and these will fill the space available to them. A fraction of these molecules will again return from vapour to the liquid state till at a certain temp. an equilibrium is attained between the vapour and liquid phases.

The pressure exerted by the vapour in such a situation at a given temp. is termed as the vapour pressure of liquid.

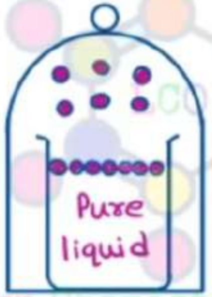


Fig:- Vapour pressure of a liquid

→ Lowering of vapour pressure:→

- In order to prepare a solution, a non-volatile solute is added to a solvent. It has been found that the vapour pressure of solution is always less than that of pure solvent.

(A) (B)

Fig:- Decrease in the vapour pressure when a solute is added to a solvent:

(A) Evaporation of molecules from the surface of pure solvent.

(B) In a solution, solute particles also occupy a part of the surface area and so reduce the number of solvent molecules at the surface that evaporate.

- Let beaker (A) contains pure solvent whereas beaker (B) contains 1 mole of non-volatile solute and one mole of solvent. Due to evaporation of liquid solvent, liquid vapours will present over the liquid phase in both beaker (A) and (B). But the relative number of solvent molecules present over the liquid surface of beaker (B) has been found to be less than that above (A). The reason for this is that some of the non-volatile molecules are also present in the liquid surface of (B). The presence of these molecules reduces the escaping surface. But evaporation of a liquid at any temperature below its boiling points depends upon the escaping surface of the liquid. Therefore, the vapour pressure of solution (B) will be less than the vapour pressure of pure solvent (A).

- Suppose p^o be the vapour pressure of pure solvent and the p the vapour pressure of solution. Then $p^o - p$ will be known as the lowering of vapour pressure.
- If the solute is volatile than vapour phase above the liquid in beaker (B) will consist of vapour of both the components. The partial vapour pressure of each component of the solution will depend upon its mole fraction in solution.

→ Raoult's law:→

- The French chemist F. Raoult studied vapour pressures of a number of binary solutions of volatile liquids, such as benzene and toluene, at constant temperature and gave the following generalisation which is known as the Raoult's law:

The partial pressure of any volatile component of a solution at any temperature is equal to the vapour pressure of the pure component multiplied by the mole fraction of that component in the solution.

- suppose a binary solution is made of n_A moles of a volatile liquid A and n_B moles of a volatile liquid B. If P_A and P_B are partial pressures of the two liquid components, then according to the Raoult's law,

$$P_A = x_A P_A^\circ \quad \text{and} \quad P_B = x_B P_B^\circ \qquad — ①$$

where x_A = mole fraction of component A, $x_A = \frac{n_A}{n_A + n_B}$

x_B = mole fraction of component B, $x_B = \frac{n_B}{n_A + n_B}$

P_A° = Vapour pressure of pure component A

P_B° = Vapour pressure of pure component B

- If the vapour behave like an ideal gas, then according to Dalton's law of partial pressures, the total vapour pressure P is given by

$$P = P_A + P_B$$

$$\text{or} \quad P = x_A P_A^\circ + x_B P_B^\circ \quad — ②$$

- In general, Raoult's law may be expressed as

$$P_i = x_i P_i^\circ \quad — ③$$

and the total vapour pressure may be expressed as

$$P = \Sigma p_i \quad — ④$$

- From the experiments, it is observed that Raoult's law is obeyed only approximately for most of the binary solutions. The law is obeyed perfectly in case of ideal solutions. Thus, A solution of two or more constituents is said to be ideal if it obeys Rault's law exactly at all concentrations and at all temperatures.
- Liquid pairs which are similar, generally form ideal solutions.
- Example of ideal solutions are -

(i) Ethylene bromide and ethylene chloride
(ii) n-hexane and n-heptane
(iii) n-butyl chloride and n-butyl bromide
(iv) Benzene and toluene
(v) Carbon tetrachloride and silicon tetrachloride

→ Vapour pressure of Ideal solutions:→

- The vapour pressure of an ideal binary solution of two components A and B having different mole fractions are shown in figure 1.
- It is evident that the graph of the partial pressure of each component against its mole fraction in the solution is a straight line and the total vapour pressure of the solution for any given composition is equal to the sum of the partial vapour pressures of the two constituents.
- The partial vapour pressure of component A is given by $x_A P_A^o$ and that of component B is given by $x_B P_B^o$. The total vapour pressure of the solution is given by $x_A P_A^o + x_B P_B^o$. Thus, when the mole fraction of B is, say, 0.80, the total vapour pressure is given by $P = 0.2\,P_A^o + 0.8\,P_A^o$ (Fig. 1).

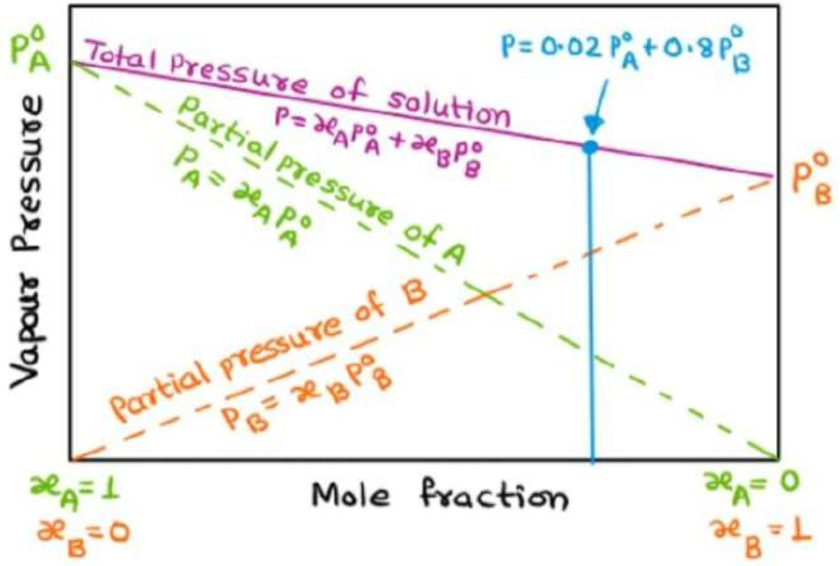


Figure:- Vapour pressure of Ideal solutions

→ Ideal and Non-ideal solutions :→

(I) Ideal solutions :→

- The solutions which obeys Raoult's law over the entire range of concentrations are known as ideal solutions.
- If two components A and B are present in binary solution then the bonds between A and B are nearly equal to A–B bond. This leads to the formation of an ideal solution.

A–B interaction = A–A and B–B interaction

- In this case, no change in intermolecular forces between two components occurs and therefore the heat change on mixing in such ideal solutions will be zero.

$$\boxed{\Delta E_{mix} = 0 \quad \text{or} \quad \Delta H_{mix} = 0}$$

- Also, in an ideal solutions the volume of the solution will equal to the sum of the volumes of the components before they are mixed. Hence the volume change on mixing is zero.

$$\boxed{\Delta V_{mix} = 0}$$

- A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour.
  - (i) Ethylene bromide and ethylene chloride
  - (ii) n-hexane and n-heptane
  - (iii) n-butyl chloride and n-butyl bromide
  - (iv) Benzene and toluene
  - (v) Carbon tetrachloride and silicon tetrachloride
  - (vi) chlorobenze and bromobenzene

(2) Non-ideal solutions:→

- The solutions which do not obey Raoult's law over the entire range of concentration are known as non-ideal solutions.
- For Non-ideal solutions –

$\boxed{\Delta E_{mix} \neq 0 \quad \text{or} \quad \Delta H_{mix} \neq 0}$ and $\boxed{\Delta V_{mix} \neq 0}$

- The vapour pressure of non-ideal solution is either higher or lower than that predicted by Raoult's law. If it is higher then solution shows positive deviation and if it is lower then solution exhibit negative deviation from Raoult's law.
- Non ideal solutions may be divided into three types–

(A) Type I:→

- These solutions show small deviations from ideal behaviour. The total vapour pressure of such solutions remain within the vapour pressure of pure constituents.
- Example:-

(i) Cyclohexane and carbon tetrachloride

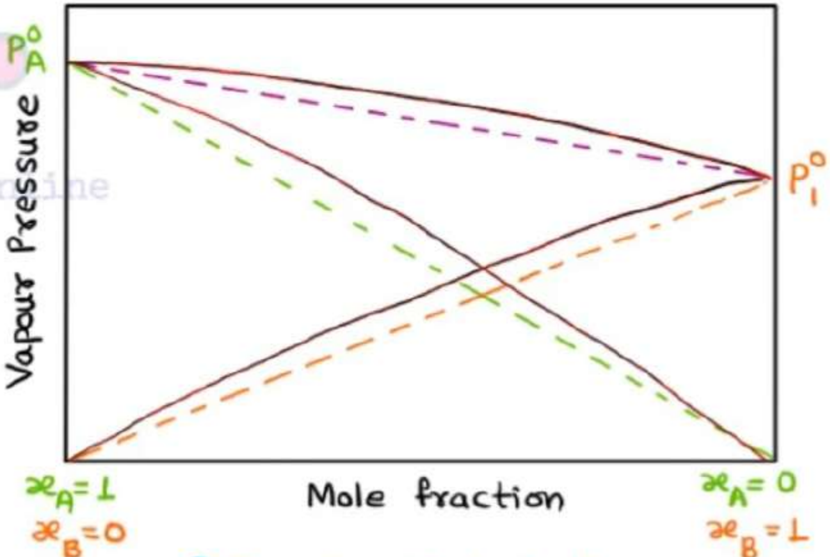


Fig:- Small deviations

(B) Type-II:→

- These show positive deviation from Raoult's law.
- In case of positive deviation-

A−B interaction < A−A or B-B interaction

This means that molecules of A or B will easier to escape than in pure state. This will increase the vapour pressure.

Example:-

(i) $(CH_3)_2CO + CS_2$

(ii) $CCl_4 + CHCl_3$

(iii) $CCl_4 + C_6H_6$

(iv) $C_6H_6 + (CH_3)_2CO$

(v) $(CH_3)CO + C_2H_5OH$

(vi) $H_2O + C_2H_5OH$

(vii) $H_2O + CH_3OH$

(viii) $CCl_4 + C_6H_5-CH_3$

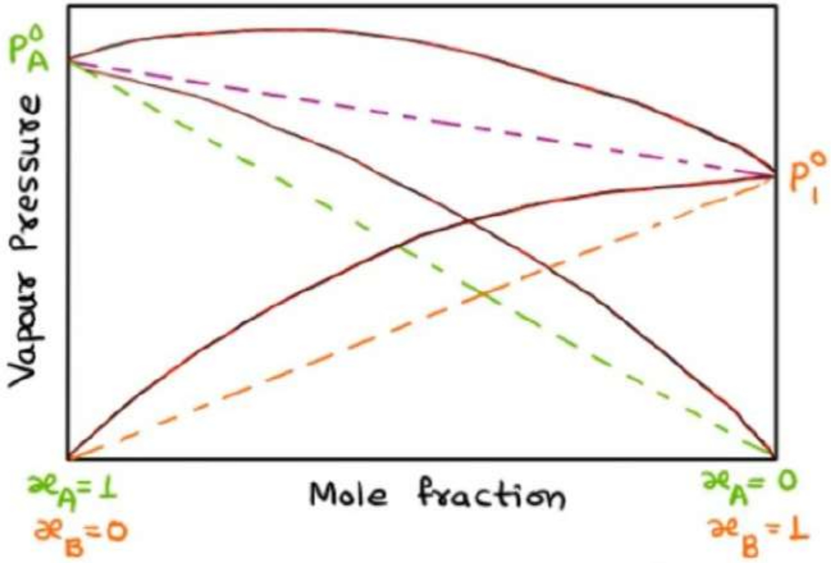


Fig:- Positive deviation

(c) Type-III:→

- These shows negative deviation from Raoult's law.
- In case of negative deviation

A-B interactions > A-A or B-B interactions

This decreases the escaping tendency of molecules for each components and as a result the vapour pressure decreases.

- Examples:-

(i) $(CH_3)_2CO + C_6H_5NH_2$
(ii) $CHCl_3 + C_6H_6$
(iii) $CHCl_3 + (C_2H_5)_2O$
(iv) $CH_3COOH + C_5H_5N$
(v) $H_2O + HCl$
(vi) $H_2O + HNO_3$
(vii) $CHCl_3 + (CH_3)_2CO$

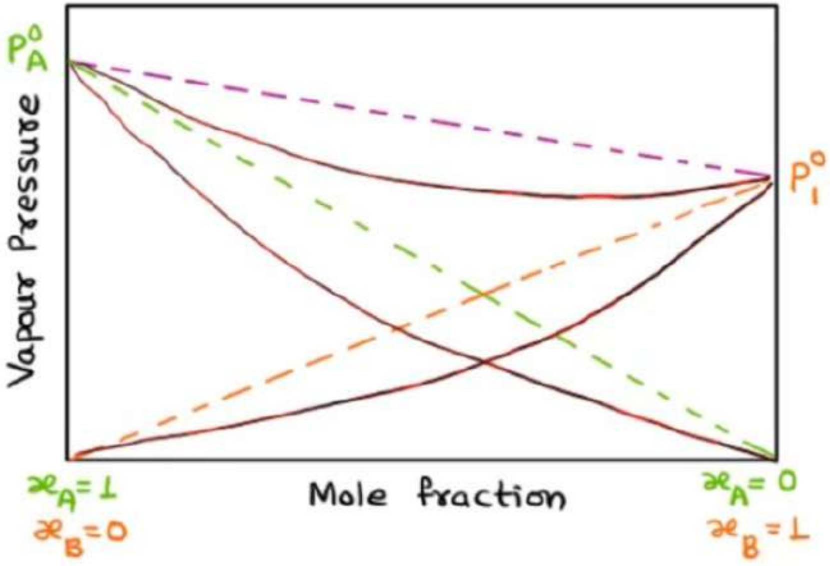


Fig :- Negative deviation

→ Activity and activity coefficient :→

- G.N. Lewis introduced the concept of activity in place of molar concentrations in case of electrolytic solutions.
- The activity is related to concentration expressed in terms of molality, i.e. in terms of moles per kg of solvent, by the expression.

$$\boxed{a = \gamma m} \quad — ①$$

where a = activity
m = molality
γ = activity coefficient

- The activity of a substance in a given system may be defined as the product of its molality and a certain factor called its activity coefficient.

- Activity coefficient :→

- Consider the dissociation of a uni-univalent electrolyte represented as:-

$$MA \rightleftharpoons M^+ + A^-$$

Applying the law of chemical equilibrium, we have

$$k = \frac{[M^+][A^-]}{[MA]} \quad — ②$$

$$\text{or} \quad k = \frac{(a_{M^+})\,(a_{A^-})}{a_{MA}} \quad — ③$$

→ Mean ionic activity coefficient :→

- It is not possible to have only one kind of ions in a solution. i.e. both anions and cations are present in a solution and solution is neutral. so, to determine activity coefficient of all ions, a new terms mean ionic activity and mean ionic activity coefficient are introduced.
- Consider ionisation of uni-univalent electrolyte MA:

$$MA \rightleftharpoons M^+ + A^+$$

The activity of cation may be denoted by a_+ and that of anion by a_-. The activity and mean ionic activity of the electrolyte, denoted by a and $a_\pm$ respectively.

$$a = (a_+)(a_-) = (a_\pm)^2 \quad — ④$$

- For any other electrolyte of type M_xA_y which ionises as

$$M_xA_y = xM^+ + yA^-$$

The activity and mean activity will be given by

$$a = (a_+)^x (a_-)^y = (a_\pm)^{x+y} \quad — ⑤$$

- If m is the initial concentration of the electrolyte M_xA_y in terms of moles per 1000 gm of the solvent, the concentration of M^+ and A^- ions would be xm and ym moles per 1000 gm of the solvent. Knowing the relation $a = \gamma m$, Eq. ⑤ may be written as –

$$a = (x\gamma_+ m)^x (y\gamma_- m)^y$$

$$\text{or} \quad a = x^x y^y \gamma_+^x \gamma_-^y m^{x+y} = x^x y^y (\gamma_\pm m)^{x+y} \quad — ⑥$$

- Where $\gamma_\pm$ is the mean molal ionic activity coefficient or simply mean activity coefficient of the electrolyte. It is, evidently, defined as

$$(\gamma_\pm)^{x+y} = (\gamma_+)^x (\gamma_-)^y \quad — ⑦$$

Thus, if a is determined experimentally, it is possible to calculate the mean activity coefficient by applying eq. ⑦. The values of x and y depends on the nature of the electrolyte.

In case of KCl, $x = 1$ and $y = 1$ therefore eq. ⑥ can be written as

$$a = 1^1 \times 1^1 (\gamma_\pm m)^{1+1}$$

$$a = (\gamma_\pm m)^2$$

For a uni-bivalent electrolyte, like K_2SO_4, $x = 2$ and $y = 1$ therefore eq. ⑥ can be written as

$$a = 2^2 \times 1^1 (\gamma_\pm m)^{2+1}$$

$$= 4 \gamma_\pm^3 m^3$$

→ Colligative properties of dilute solutions:→

→ Dilute solution:→

- The solution in which quantity of solute is relatively very small is called dilute solution.

→ Colligative properties:→

- Colligative : from Latin : co means together : ligare means to bind.
- Those properties of the solutions which depend only upon the total number of molecules of the solute per unit volume and not on its chemical nature are colligative properties

OR

Colligative properties are those which depend entirely upon the number of particles of the solute dissolved in a known volume of a given solution and not at all upon the nature (i.e. chemical composition or constitution) of the solute.

- These properties, in fact, depend upon the nature of the solvent. The colligative properties can thus be rightly regarded as the properties of the solvent in a given solution.
- In the study of colligative properties, the solute taken as non-volatile.
- The various colligative properties are:-

1. Lowering of vapour pressure.
2. Osmotic pressure
3. Elevation of boiling point
4. Depression of freezing point

- The colligative properties are widely used for the determination of molecular masses of substances.

→ Mathematical expression:→

- If two solutions are made from different components, they may show identical values of colligative properties which are dependent only on mole fractions in the solutions. Thus

$$\text{Colligative property measured} \propto \text{Mole fraction of the solute}$$

- Suppose a system of two components A (Solvent) and B (Solute) is considered.

$$\text{Number of moles of solvent, } n_A = \frac{W_A}{M_A}$$

$$\text{Number of moles of solute, } n_B = \frac{W_B}{M_B}$$

$$\text{mole fraction of solvent, } x_A = \frac{n_A}{n_A + n_B} \text{ and mole fraction of solute, } x_B = \frac{n_B}{n_A + n_B}$$

But according to definition,

$$\text{Colligative property} \propto \frac{n_B}{n_A + n_B}$$

$$\text{or} \quad \text{Colligative property} = \gamma \frac{n_B}{n_A + n_B} = \gamma \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \quad \text{— ①}$$

γ = proportionality constant which depends on nature of colligative property.

- Eq. ① is very useful because it can be used for calculating the value of any of the involved factors provided the value of all the rest are known.

→ Relative lowering of vapour pressure :→

- The vapour pressure of a solvent in solution is less than that of the pure solvent.
- According to Raoult's law, the lowering of vapour pressure depends only on the concentration of the solute particles and it is independent of their identity.
- The relation b/w vapour pressure of solution, mole fraction and vapour pressure of pure solvent is given by the following equation -

$$P_1 = x_1 P_1^0 \quad — \quad ①$$

The reduction in the vapour pressure (ΔP_1) is given as

$$\Delta P_1 = P_1^0 - P_1$$

or $$\Delta P_1 = P_1^0 - P_1^0 - x_1$$

or $$\Delta P_1 = P_1^0 (1 - x_1) \quad — \quad ②$$

we know that

$$x_1 + x_2 = 1$$

or $$x_2 = 1 - x_1$$

Eq. ② reduces to

$$\Delta P_1 = x_2 P_1^0 \quad — \quad ③$$

In a solution containing several non-volatile solutes, the lowering of vapour pressure depends on the sum of the mole fraction of different solutes.

Equation ③ can be written as

$$\frac{\Delta P_1}{P_1^\circ} = \frac{P_1^\circ - P_1}{P_1^\circ} = x_2 \quad — ④$$

$\frac{\Delta P_1}{P_1^\circ} = \frac{P_1^\circ - P_1}{P_1^\circ}$ is called relative lowering of vapour pressure and is equal to mole fraction of solute.

Equation ④ can be written as

$$\frac{P_1^\circ - P_1}{P_1^\circ} = \frac{n_2}{n_1 + n_2} \quad \left(\because x_2 = \frac{n_2}{n_1 + n_1}\right) \quad \begin{cases} n_1 = \text{moles of solvent} \\ n_2 = \text{moles of solute} \end{cases}$$

For dilute solutions

$n_2 <<< n_1$, hence n_2 = negligible

$$\frac{P_1^\circ - P_1}{P_1^\circ} = \frac{n_2}{n_1} \quad — ⑤$$

or $$\frac{P_1^\circ - P_1}{P_1^\circ} = \frac{W_2/M_2}{W_1/M_1} \quad \left(\because n = \frac{W}{M}\right)$$

or $$\boxed{\frac{P_1^\circ - P_1}{P_1^\circ} = \frac{W_2 \times M_1}{M_2 \times W_1}} \quad — ⑥$$

where W_1 = Mass of solvent
M_1 = Molar mass of solvent
W_2 = Mass of solute
M_2 = Molar mass of solute

- From eq. ⑥, knowing all other quantities, the molar mass of solute (M_2) can be calculated.

→ Elevation of boiling point :→

- The vapour pressure of liquid increases with increase of temp. and it boils at the temp. at which its vapour pressure is equal to the atomospheric pressure.

Example:- Boiling point of water = 373.15 K (100°C)

At this temp. vapour pressure of water = 1.013 bar (1 atm)

- The vapour pressure of the solvent decreases in the presence of non-volatile solute and vapour pressure is increased by raising the temp above the boiling point of the pure solvent.

Example:- The vapour pressure of aq. solution of sucrose is less than 1.013 bar at 373.15 K. In order to increase vapour pressure, this solution must be boiled above the boiling temp. of the solvent (water).

Thus, the boiling point of a solution is always higher than that of boiling point of the pure solvent in which the solution is prepared.

Example:- A solution of 1 mol of sucrose in 1000 ml of water boils at 373.52 K at one atm pressure.

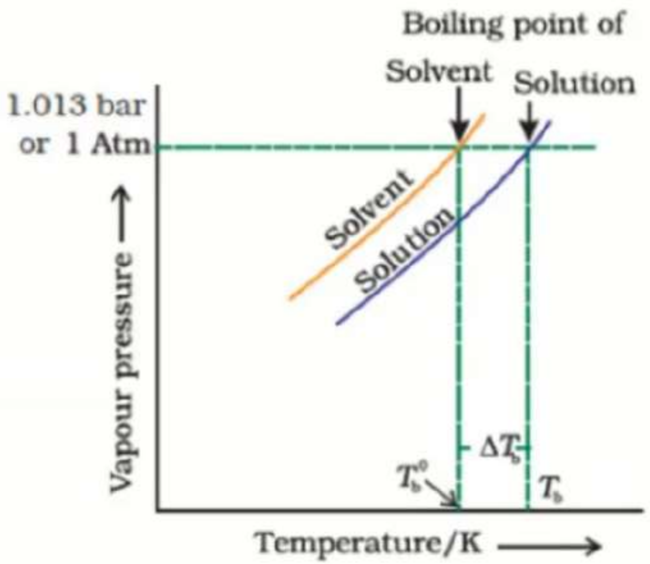
- Similar to lowering of vapour pressure, the elevation of boiling point also depends on number of solute molecules rather than their nature.

Let

Boiling point of pure solvent = T_b°
and boiling point of the solution = T_b
Then increase of boiling point is

$$\Delta T_b = T_b - T_b^\circ \quad — ①$$

Eq. ① is called elevation of boiling point



- For dilute solutions, the elevation in boiling point (ΔT_b) is directly proportional to the molal concentration (molality) of the solute in a solution.

$$\Delta T_b \propto m \quad — ②$$

or $$\Delta T_b = K_b m \quad — ③$$

where m = molality
K_b = Proportionality constant, called boiling point elevation constant or molal elevation constant (Ebullioscopic constant)

unit of K_b = K kg mol^{-1}

If weight of solute = W_2 g, weight of solvent = W_1 g
Molar mass of solute = M_2
then molality of solution

$$m = \frac{W_2/M_2}{W_1/1000} = \frac{W_2 \times 1000}{M_2 \times W_1} \quad — ④$$

Substituting value of m in eq. ③

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1} \quad — ⑤$$

or

$$M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1} \quad — ⑥$$

Thus, in order to determine M_2, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined experimentally for a known solvent whose K_b value is known.

→ Depression of freezing point: →

- The lowering of vapour pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent.
- At the freezing point of a substance, the solid phase is in dynamic equilibrium with the liquid phase. Thus, the freezing point of a substance may defined as the temp at which the vapoure pressure of the substance in its liquid phase is equal to its vapour phase in the solid phase.
- A solution will freeze when its vapour pressure equals the vapour pressure of the pure solvent.
- According to the Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and become equal to that of solid solvent at lower temp. Thus, the freezing point of solvent decreases.

- Let

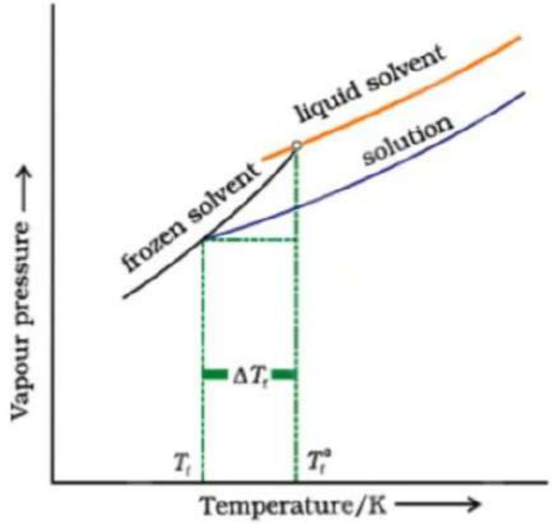
Freezing point of pure solvent = T_f^{o}

and freezing point of the solution = T_f

Then decrease in freezing point is

$$\Delta T_f = T_f^{o} - T_f \quad \text{—} ①$$

Eq. ① is called depression of freezing point



- For dilute solutions, the depression of freezing point (ΔT_f) is directly proportional to the molal concentration (molality) of the solute in a solution.

$$\Delta T_f \propto m \quad — ②$$

or $$\Delta T_f = k_f m \quad — ③$$

where m = molality

k_f = Proportionality constant, called freezing point depression constant or molal depression constant (Cryoscopic constant)

unit of k_f = K kg mol^{-1}

If weight of solute = W_2 g, weight of solvent = W_1 g

Molar mass of solute = M_2

then molality of solution

$$m = \frac{W_2/M_2}{W_1/1000} = \frac{W_2 \times 1000}{M_2 \times W_1} \quad — ④$$

Substituting value of m in eq. ③

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1} \quad — ⑤$$

or $$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1} \quad — ⑥$$

Thus, in order to determine M_2, known mass of solute in a known mass of the solvent is taken and ΔT_f is determined experimentally for a known solvent whose K_f value is known.

- The values of K_f and K_b can be determined from the following relations:-

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta H_{fus}}$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta H_{vap}}$$

where R = Gas constant

M_1 = Molar mass of solvent

T_f = Freezing point of pure solvent (K)

T_b = Boiling point of pure solvent (K)

ΔH_{fus} = Enthalpy of fusion

ΔH_{vap} = Enthalpy of vapourisation.

→ Osmosis:→

- When a solution is separated from its solvent by a semipermiable membrane, the solvent molecules pass through it into solution to have uniform concentration on both sides of the membrane.
- The phenomenon of the flow of solvent molecules through a semipermeable membrane from pure solvent to the solution is called osmosis.

"OR"

The movement of molecules from the region of lower concentration into region of higher concentration solution through a semipermeable mebrane is called osmosis.

→ Example:→

- If we take two eggs of equal size whose outer shells have been removed and put one of them in distilled water and the other in saturated salt solution then after few hours the egg placed in water swells up while one in salt solution shrinks. It is due to fact that in case of egg placed in distilled water, the water enters the concentrated egg fluid while in other case it goes out of the egg into more concentrated solution to have uniform concentration in and out.

— Osmosis differs from diffusion in the following respect :-

Osmosis	Diffusion
1. There is a flow of solvent into the solution through a semipermeable membrane.	1. There is a flow of both the solvent and the solute and no semipermeable membrane is required.
2. Solvent flows from the solution of lower concentration to solution of higher concentration.	2. Solution flows from higher concentration to lower concentration until an equilibrium in concentration is achieved.

→ Semipermeable membrane :→ (SPM)

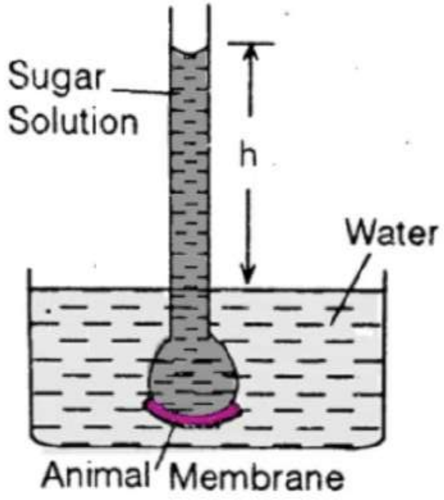
— A membrane which allows the solvent but not the solute molecules to pass through it is known as semipermeable membrane.

— Example:-

1. The membrane surrounding plant and animal cell.
2. Pig bladder
3. A layer of phenol saturated with water
4. The gelatinous precipitates of calcium phosphate and copper ferrocyanide

→ Osmotic pressure :→

- The spontaneous flow of solvent into a solution or from a more dilute to a concentrated solution through a semipermeable membrane is known as osmosis.
- In order to understand osmosis, we take a thistle funnel filled with sugar solution, whose lower end is tied with an animal membrane. Now we placed in a beaker which contain distilled water.



Due to osmosis, water will flow into funnel through the membrane and liquid level rises in funnel.

As the liquid rises in the tube, a hydrostatic pressure is developed. The pressure increases the tendency for the solvent molecules to move from the solution back into the pure solvent and operates against the force causing osmosis. As a result, an equilibrium condition is finally reached in which the hydrostatic pressure is sufficient to prevent further diffusion.

That hydrostatic pressure acting on the solution side of the semipermeable membrane that is just sufficient to prevent osmosis is termed as the osmotic pressure of the solution.

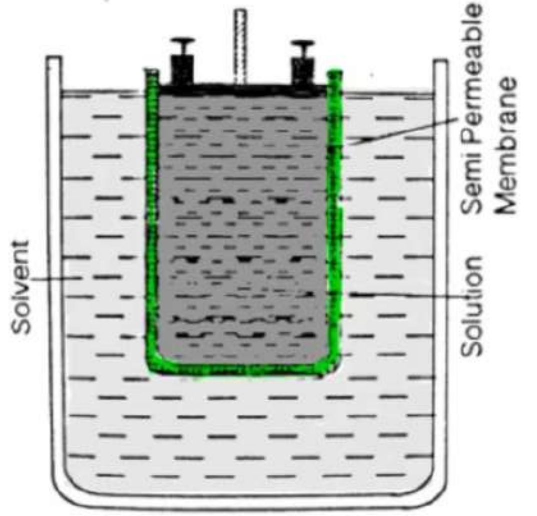
If liquid rises to a hight 'h', then

osmotic pressure = hdg

where d = density of the solution

g = accelaration due to gravity

→ Another definition of osmotic pressure:→



- Suppose a solution is kept in a cup whose walls contain a semipermeable membrane. The cup is tightly closed by a rubber piston. Then, this cup is kept in a bigger beaker containing water (solvent).

  Due to osmosis, the water will move from the beaker into the cup through the semipermeable membrane. This tendency can be overcome by applying pressure on the solution by keeping increasing weights on the piston. As soon as a proper weight is placed, no osmosis take place.

  This excess pressure acting on the solution which prevents osmosis is known as osmotic pressure of the solution.

→ Isotonic solutions:→

- The solutions having same osmotic pressure are known as isotonic solutions. when such solutions are separated by semipermeable membrane, no osmosis takes place.
- Isotonic solutions have same molar concentrations.
- If an unknown solution, has lower osmotic pressure than the given known solution, then that unknown solution is called hypotonic solution but in case the unknown solution has higher osmotic pressure it is called hypertonic solution.

→ Laws of osmotic pressure :→ (Van't Hoff's Theory of dilute solutions)

- From measurement of osmotic pressure Van't Hoff observed that certain laws which are obeyed by gases are also obeyed by dilute solutions.

(i) Boyle Van't Hoff law :→

- Pfeffer's results indicate that the osmotic pressure of the solution is directly proportional to its concentration.

$$\therefore \quad \boxed{P \propto C \propto \frac{1}{V}} \text{ — ①}$$

where
P = Osmotic pressure
C = concentration in moles per litre
V = Volume of solution containing 1 mol of solute

PV = constant (at constant T)

In other words " At constant temperature, the product of osmotic pressure and volume is constant."

This is exactly similar to Boyle's law for gases.

(ii) Pressure temperature Law :→

- If the concentration of solution is kept the same, the osmotic pressure varies directly as absolute temperature.
- In other words, " At constant volume, the osmotic pressure of solution is directly proportional at absolute temperature.

$\boxed{P \propto T}$ — ② * This is similar to Charle's law for gases.

(iii) General equation for solutions:→

- From the above two laws:-

$$P \propto \frac{1}{V} \quad \text{and} \quad P \propto T$$

$$\therefore \quad P \propto \frac{T}{V} \quad \text{OR} \quad PV \propto T$$

Hence $\boxed{PV = ST}$ — ③

where S = Solution constant

Equation ③ is exactly similar to general gas equation and the value of S (0.0821 litre-atm) corresponds about exactly with R obtained for gases.

(iv) Avagadro Van't Hoff law:→

- Equal volumes of solutions containing equal number of solute molecules, excert same osmotic pressure at same temperature. This is similar to Avogadro's law of gases.
- On the basis of analogous behaviour of dilute solutions to gases, Van't Hoff gave a theory of dilute solution in 1885 called Van't Hoff's theory of dilute solutions.
- According to this theory," The solute molecules in a dilute solution play the same role as is as played by the gas molecules in a gas, the osmotic pressure being analogue of gas pressure.

→ Determination of molecular weight from osmotic pressure:→

– According to Van't Hoff, dilute solution obey the general gas equation.

$$PV = n_2ST \quad — ①$$

where P = osmotic pressure

V = Volume in literes

S = Solution constant (0.0821 litre-atm)

T = Absoulte temperature

n_2 = Number of moles of solute

From equation ①

$$P = \frac{n_2}{V}ST \quad \text{OR} \quad P = CST \quad — ② \quad \left[\because C = \frac{n_2}{V}\right]$$

C = molar concentration of the solute

If weight of solute = w_2 g

and molar mass of the solute = M_2

then $n_2 = \frac{W_2}{M_2}$

and eq. ② becomes

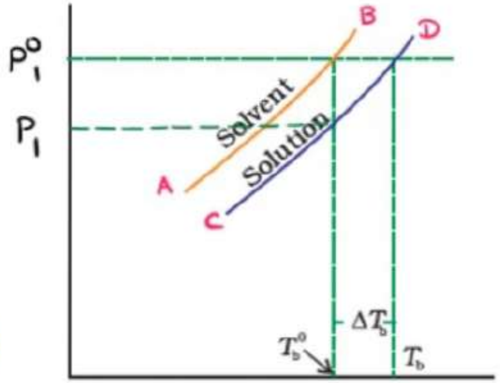
$$P = \frac{W_2ST}{M_2V} \quad — ③ \qquad \text{or} \qquad M_2 = \frac{W_2ST}{PV} \quad — ④$$

Thus, knowing the quantities of W_2, T, V and P, we can calculate the molar mass of solute.

- This method is widely used to determine molar masses of proteins, polymers and other macromolecules.
- In this method molarity is used instead of molality.

→ Thermodynamic derivation of relation between molecular weight and elevation in boiling point :→

- A liquid starts boiling at the temperature when its vapour pressure is equal to the atomspheric pressure. But the vapour pressure of a liquid is lowered by the addition of a non-volatile solute. Therefore the boiling point of a solution must be higher than that of pure solvent. In other words, the boiling point of a solvent gets elevated by the addition of non-volatile solute to it.
- From Clausius-Clapeyron's equation for liquid vapour equilibrium



$$\ln \frac{P_1^o}{P_1} = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_b^o} - \frac{1}{T_b}\right] \quad — ①$$

where P_1 = Vapour pressure of solution
P_1^o = Vapour pressure of pure solvent
T_b = Boiling point of solution
T_b^o = Boiling point of pure solvent
R = Gas constant
ΔH_{vap} = Molar heat of vaporisation

Eq. ① can be written as

$$\ln \frac{P_1^o}{P_1} = \frac{\Delta H_{vap}}{R}\left[\frac{T_b - T_b^o}{T_b^o T_b}\right] \quad — ②$$

We know that elevation in boiling point

$$\Delta T_b = T_b^o - T_b$$

For dilute solutions elevation in boiling point is very less

$$T_b^o \approx T_b \quad \text{therefore} \quad T_b^o T_b = T_b^{o2}$$

So equation ② becomes

$$\ln \frac{P_1^o}{P_1} = \frac{\Delta H_{vap}}{R} \cdot \frac{\Delta T_b}{T_b^{o2}} \quad — ③$$

By Raoult's law, we have

$$\frac{P_1^o - P_1}{P_1^o} = x_2$$

or $$1 - \frac{P_1}{P_1^o} = x_2 \quad \text{or} \quad \frac{P_1}{P_1^o} = 1 - x_2$$

or $$\ln \frac{P_1}{P_1^o} = \ln(1 - x_2) \quad — ④$$

For dilute solution $\ln(1-x_2) \approx -x_2$ so equation ④ becomes

$$\ln \frac{P_1}{P_1^o} = -x_2 \quad \text{or} \quad \ln \frac{P_1^o}{P_1} = x_2 \quad — ⑤$$

From equation ③ and ⑤

$$x_2 = \frac{\Delta H_{vap}}{R} \cdot \frac{\Delta T_b}{T_b^{o2}} \quad \text{OR} \quad \Delta T_b = \frac{R T_b^{o2}}{\Delta H_{vap}} \cdot x_2 \quad — ⑥$$

we know that

$$x_2 = \frac{n_2}{n_1 + n_2} \quad \text{or} \quad x_2 = \frac{n_2}{n_1} \quad (\text{for dilute solutions } n_2 <<< n_1)$$

No. of moles of solute $n_2 = \frac{W_2}{M_2}$

No. of moles of solvent $n_1 = \frac{W_1}{M_1}$

where
W_2 = mass of solute
W_1 = mass of solvent
M_2 = molar mass of solute
M_1 = molar mass of solvent

Therefore

$$x_2 = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}} \quad \text{or} \quad x_2 = \frac{W_2 M_1}{M_2 W_1} \quad — ⑦$$

from eq. ⑥ & ⑦

$$\Delta T_b = \frac{R T_b^{o2}}{\Delta H_{vap}} \cdot \frac{W_2 M_1}{M_2 W_1} \quad — ⑧$$

$$\text{or} \quad \Delta T_b = \frac{R T_b^{o2} W_2}{L_e M_2 W_1} \quad — ⑨$$

where L_e = latent heat of vapourisation per gram of solvent $= \frac{\Delta H_{vap}}{M_1}$

If one mole of solute is dissolved in 1000g of solvent then

$$n_2 = \frac{w_2}{M_2} = 1 \quad \text{and} \quad w_1 = 1000\,\text{gm}$$

In this case equation ⑨ becomes

$$\Delta T_b = \frac{R T_b^{o^2}}{L_e \times 1000} \quad \text{—} \quad ⑩$$

The molal elevation constant, K_b of the solvent is gives as

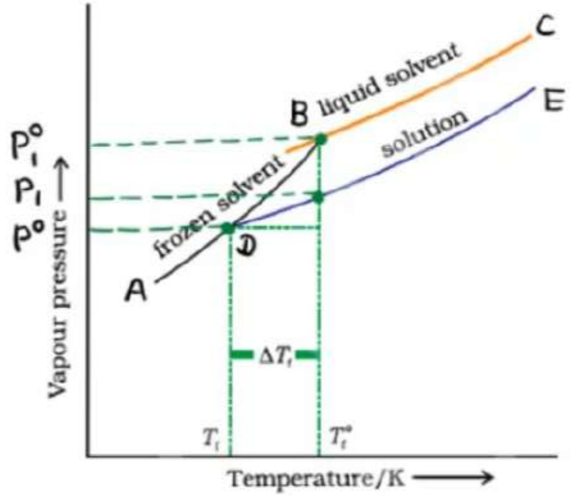
$$K_b = \frac{R T_b^{o^2}}{L_e \times 1000} \text{ — } ⑪ \left(\because \Delta T_b = K_b m \text{ , if } m = 1 \text{ then } \Delta T_b = K_b\right)$$

As all the quantities R, $T_b^{o^2}$ and L_e are constant then K_b is constant for a given solvent.

Eq. ⑪ gives relation between molal elevation constant of liquid, it heat of vaporisation and boiling point.

→ Thermodynamic derivation of relation between molecular weight and depression in freezing point: →

- The freezing point of a substance may be defined as the temperature at which its solid and liquid forms have same vapour pressure. But the vapour pressure of a solvent is lowered by the addition of non-volatile solute. Therefore the freezing point of the solution will always be lower than that of the pure solvent. Hence it can be said that the freezing point of the solvent get depressed by the addition of a non-volatile solute to it.
- Consider curve BA (solid ⇌ vapour curve) and apply Clausius-Clapeyron equation on this curve



$$\ln \frac{P_1^o}{p^o} = \frac{\Delta H_{sub}}{R}\left[\frac{1}{T_f} - \frac{1}{T_f^o}\right] \text{ — } ①$$

$$\ln \frac{P_1^o}{p^o} = \frac{\Delta H_{sub}}{R}\left[\frac{T_f^o - T_f}{T_f T_f^o}\right] \text{ — } ②$$

where
P_1 = Vapour pressure of solution at T_f^o
P_1^o = Vapour pressure of pure solvent
p^o = Vapour pressure of Solution at T_f
T_f = Freezing point of solution
T_f^o = Freezing point of pure solvent
R = Gas constant
ΔH_{sub} = Molar heat of sublimation

We know that depression in freezing point

$$\Delta T_f = T_f^{\circ} - T_f$$

for dilute solution depression in freezing point is very less

$$T_f \approx T_f^{\circ} \quad \text{or} \quad T_f T_f^{\circ} = T_f^{\circ 2}$$

So equation ② becomes

$$\ln \frac{P_1^{\circ}}{P^{\circ}} = \frac{\Delta H_{sub}}{R} \cdot \frac{\Delta T_f}{T_f^{\circ 2}} \text{———} ③$$

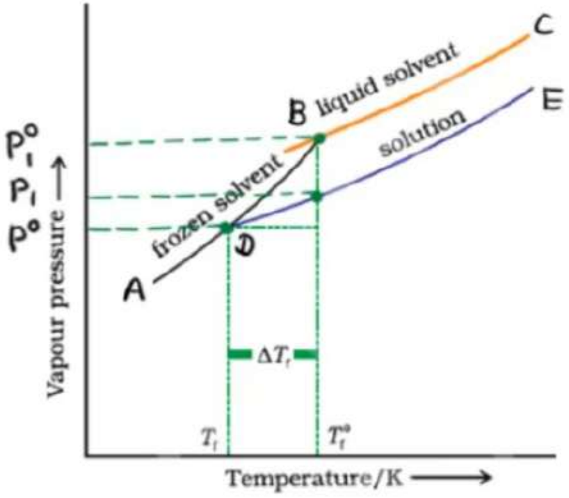
- Consider curve DE (liquid ⇌ vapour curve) and apply Clausius-Clapeyron equation on this curve

$$\ln \frac{P_1}{P^{\circ}} = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_f} - \frac{1}{T_f^{\circ}}\right] \text{———} ③$$

$$\ln \frac{P_1}{P^{\circ}} = \frac{\Delta H_{vap}}{R}\left[\frac{T_f^{\circ} - T_f}{T_f T_f^{\circ}}\right] — ④$$

We know that $\Delta T_f = T_f^{\circ} - T_f$ and $T_f T_f^{\circ} = T_f^{\circ 2}$. so eq. ④ becomes

$$\ln \frac{P_1}{P^{\circ}} = \frac{\Delta H_{vap}}{R} \cdot \frac{\Delta T_f}{T_f^{\circ 2}} \quad — ⑤$$



For Solid $\rightleftharpoons$ liquid equilibrium

on substracting equation ⑤ from ③

$$\ln\frac{P_1^0}{p^0} - \ln\frac{P_1}{p^0} = \frac{\Delta H_{sub}}{R}\cdot\frac{\Delta T_f}{T_f^{o2}} - \frac{\Delta H_{vap}}{R}\cdot\frac{\Delta T_f}{T_f^{o2}}$$

$$\ln P_1^o - \ln P_1 = \frac{\Delta T_f}{RT_f^{o2}}\left(\Delta H_{sub} - \Delta H_{vap}\right)$$

$$\ln\frac{P_1^o}{P_1} = \frac{\Delta H_{fus}}{R}\cdot\frac{\Delta T_f}{T_f^{o2}} \quad -⑥ \quad (\because \Delta H_{fus} = \Delta H_{sub} - \Delta H_{vap})$$

By Raoult's law, we have

$$\frac{P_1^o - P_1}{P_1^o} = x_2$$

or $$1 - \frac{P_1}{P_1^o} = x_2 \quad \text{or} \quad \frac{P_1}{P_1^o} = 1 - x_2$$

or $$\ln\frac{P_1}{P_1^o} = \ln(1-x_2) \quad - ⑦$$

For dilute solution $\ln(1-x_2) \simeq -x_2$ so equation ⑦ becomes

$$\ln\frac{P_1}{P_1^o} = -x_2 \quad \text{or} \quad \ln\frac{P_1^o}{P_1} = x_2 \quad - ⑧$$

From equation ⑥ and ⑧

$$x_2 = \frac{\Delta H_{fus}}{R} \cdot \frac{\Delta T_f}{T_f^{o2}} \quad \text{OR} \quad \Delta T_f = \frac{R\,T_f^{o2}}{\Delta H_{fus}} \cdot x_2 \quad — ⑨$$

we know that

$$x_2 = \frac{n_2}{n_1+n_2} \quad \text{or} \quad x_2 = \frac{n_2}{n_1} \quad (\text{for dilute solutions } n_2 <<< n_1)$$

No. of moles of solute $n_2 = \frac{W_2}{M_2}$

No. of moles of solvent $n_1 = \frac{W_1}{M_1}$

where

W_2 = mass of solute

W_1 = mass of solvent

M_2 = molar mass of solute

M_1 = molar mass of solvent

Therefore

$$x_2 = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}} \quad \text{or} \quad x_2 = \frac{W_2 M_1}{M_2 W_1} \quad — ⑩$$

From eq. ⑨ & ⑩

$$\Delta T_f = \frac{R\,T_f^{o2}}{\Delta H_{fus}} \cdot \frac{W_2 M_1}{M_2 W_1} \quad — ⑪$$

or

$$\Delta T_f = \frac{R\,T_f^{o2}\,W_2}{L_f\,M_2 W_1} \quad — ⑫$$

where L_f = latent heat of fusion per gram of solvent $= \frac{\Delta H_{fus.}}{m_1}$

If one mole of solute is dissolved in 1000g of solvent then

$$n_2 = \frac{w_2}{M_2} = 1 \quad \text{and} \quad w_1 = 1000\,\text{gm}$$

In this case equation ⑫ becomes

$$\Delta T_f = \frac{R T_f^{\circ 2}}{L_f \times 1000} \quad \text{—} \quad ⑬$$

The molal depression constant, K_f of the solvent is gives as

$$K_f = \frac{R T_f^{\circ 2}}{L_f \times 1000} \text{—} ⑭ \left(\because \Delta T_f = K_f m \,,\ \text{if } m = 1 \text{ then } \Delta T_f = K_f \right)$$

As all the quantities R, $T_f^{\circ 2}$ and L_f are constant then K_f is constant for a given solvent.

Eq. ⑭ gives relation between molal depression constant of liquid, it heat of fusion and freezing point.

→ Experimental methods for determining lowering of vapour pressure :→

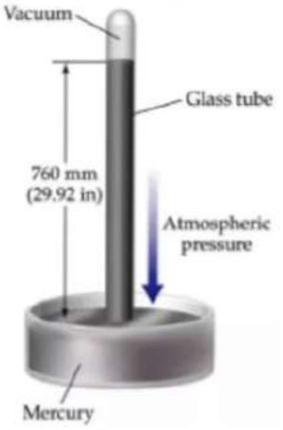
1. Barometric Method :→

- Raoult measured the individual vapour pressure of a liquid and then the solution by this metho He introduced the liquid or the solution into Toricellian vacuum of a barometer tube and measured the depression of the mercury level.

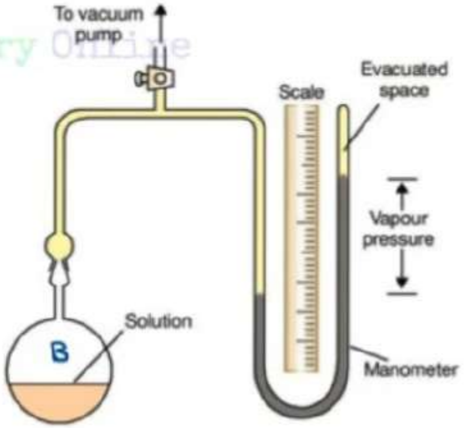
  This method is neither practicable nor accurate as lowering of vapour pressure has been too small.

2. Manometric Method :→

- The vapour pressure of a liquid or solution can be conveniently determined with the help of a manometer. The bulb B is filled with liquid or solution. The air in the connecting tube is the removed with a vaccum pump. If the stopclock is closed, the pressure inside is due only to the vapour evoporating from the solution or liquid. This method is generally used for aqueous solution. The manometric liquid can be mercury or n-butyl phthalate which has low density and low volatility.



Toricelli
Barometer



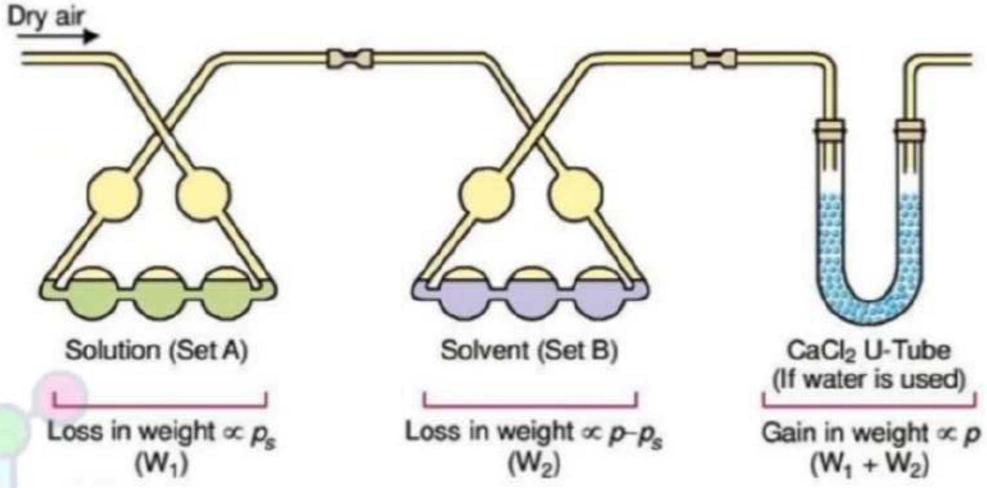
Mercury
Manometer

3. Ostwald and Walker's dynamic method (Gas saturation method):→

- This apparatus contains two sets of bulbs-

(a) set A (b) set B

- Each set is weight separetly. A slow stream of dry air is then drawn by suction pump through the set of two bulbs. At the end of operation, two sets of bulbs are reweighed. From the loss of weight in each of the two sets, the lowering of vapour pressure is calculated. The temp of the air, the solution and the solvent must be kept constant throughout.



→ Calculation:-

Loss in weight of set A, $W_1 \propto P_s$ — ① where P_s = Vapour pressure of solution

Loss in weight of set B, $W_2 \propto P - P_s$ — ②

on adding equations ① and ②

$$W_1 + W_2 \propto P_s + P - P_s$$

or $W_1 + W_2 \propto P$ — ③

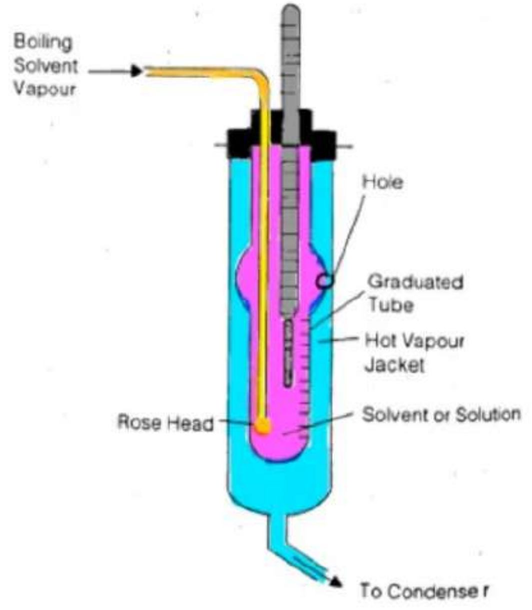
Dividing equation ② by ③

$$\frac{P - P_s}{P} = \frac{W_2}{W_1 + W_2} \quad \text{— ④}$$

→ Measurment of boiling point elevation:→

→ Landsberger-Walker Method:→

— This method was introduced by Landsberger and modified by Walker.



Apparatus:→

— Apparatus consist of following parts -

(i) An inner tube with a hole in its side and graduated in ml.

(ii) A boiling flask which sends solvent vapour into graduated tube through a 'rosehead' (a bulb with several holes).

(iii) An outer tube which receives hot solvent vapour issuing from the side-hole of the inner tube.

(iv) A therometer reading to 0.01K, dipping in solvent or solution in the inner tube.

— Procedure:→

Pure solvent is kept in the graduated tube and vapour of the same solvent boiling in a separate flask is passed into it. The vapour causes the solvent in the tube to boil by its latent heat of condensation. When the solvent starts boiling and temperature becomes constant, it boiling point is recorded.

Now the supply of vapour is temporarily cut off and a weight pallet of the solute is dropped into the solvent in the inner tube. The solvent vapour is again allowed to pass through until the boiling point of the solution is reached and this is recorded.

The solvent vapour is then cut off, thermometer and rosehead raised out of solution, and the volume of the solution read.

- From the difference in the boiling points of solvent and solution, the molecular weight of the solute (M) can be found out by using the expression.

$$M = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

Where K_b = Molal elevation constant
ΔT_b = Elevation in boiling point
W_1 = Weight of solvent
W_2 = weight of solute

→ Measurement of boiling point elevation:→

- Cottrell's method:→

— This method was developed by Cottrell in 1910 and better than Landsberger - Walker method.

- Apparatus:→

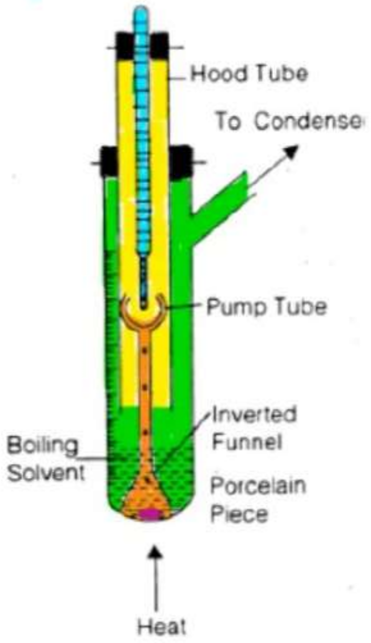
- Apparatus consist of following parts:→

(i) A graduated boiling tube containing solvent or solution.

(ii) A reflux condenser which returs the vaporised solvent to the boiling tube.

(iii) A thermometer reading to 0.01 K, enclosed in a glass hood.

(iv) A small inverted funnel with a narrow stem which branches into three jets projecting at thermometer bulb.



- Bakmann thermometer:→

- It is a differential thermometer. It is designed to measure small changes in temperature and not the temperature itself.

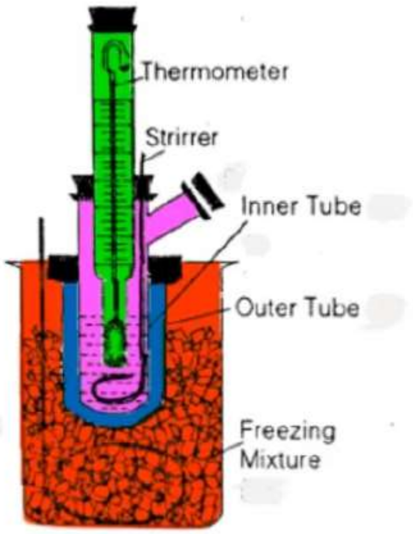
- Procedure:→

— Solvent is kept in the boiling tube with a porcelain piece lying in it. It is heated on a small flame (micro burner). As the solution starts boiling, solvent vapour arising from the porcelain piece pumps the boiling liquid into the narrow stem. Thus a mixture of solvent vapour and boiling liquid is continuously sprayed around the thermometer bulb. The temp. soon becomes constant and the boiling point of pure solvent is recorded.

- Now a weighed pellet of the solute is added to the solvent and boiling point of the solution noted as the temperature becomes steady. Also, the volume of the solution in the boiling tube can be noted.
- The difference of boiling temperatures of the solute and solvent gives the elevation of boiling point. While calculating the molecular weight of solute, the volume of solution is converted into mass by multiplying with density of solvent at its boiling point.

→ Measurement of freezing point depression:→

- Beckmann's Method:→



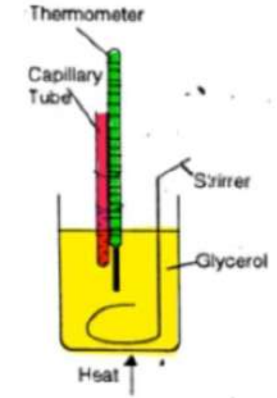
- This is most widely used method and gives sufficient accurate results.
- The apparatus consist of a big tube having a side tube for introducing the solute.
- It is fitted up with stirrer and Beckmann's thermometer.
- The tube is filled with a definite weight of solvent, sufficient to dip the thermometer bulb and is suspended in another outer tube wide enough to provide sufficient air space between them.
- This whole system is placed in an outer vessel containing freezing mixture whose temp is about 5° below the freezing point of the pure solvent.
- The space between the two test tubes serves as an air jacket and prevent direct heat conduction and consequent super cooling.
- On placing the tubes in the freezing mixture the temp of the solvent in the inner tube gradually falls and due to super cooling even goes below the true freezing point of the solvent. on rapid stirring, however, the solid begins to separate and mercury risely rapidly in the thermometer due to latent heat set free and finally become stedy. The temperature is noted which is freezing point of pure solvent.
- The pellet of known weight of solute is introduced in solvent and freezing point is determined as before.

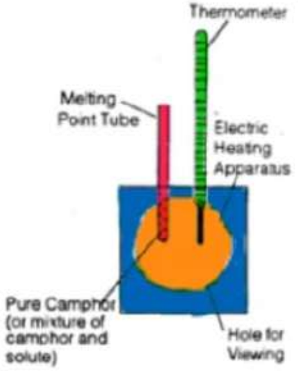
- The difference in freezing points of solute and solvent is equal to depression in freezing point. By substituting the values in the equation, the molecular weight of the solute can be calculated.
- <u>Limitations</u>:→
- This method cannot be applied to insoluble or sparingly soluble substance.
- This method is not applicable to volatile substance.
- The concentration of solution must be very low.
- This method gives abnormal value for substances which associate or dissociate in solution.

→ Measurement of freezing point depression: →

→ Rast's camphor method: →

- This method is discovered by Rast (1922) and is used for the molecular weights of solutes which are soluble in molten camphor.
- The freezing point depressions are so large that an ordinary thermometer can be used.
- Pure camphor is powdered and introduced into capillary tube which is sealed at one end. This is tied along a thermometer and heated in a glycerol bath. The melting point of camphor is recorded. Then a weighed amount of solute and camphor (about 10 times as much) are melted in test tube with the open end sealed. The solution of solute in camphor is cooled in air. After solidification, the mixture is powdered and introduced into a capillary tube which is sealed. Its melting point is recorded as before. The difference in melting point of camphor and the mixture, gives the depression of freezing point.

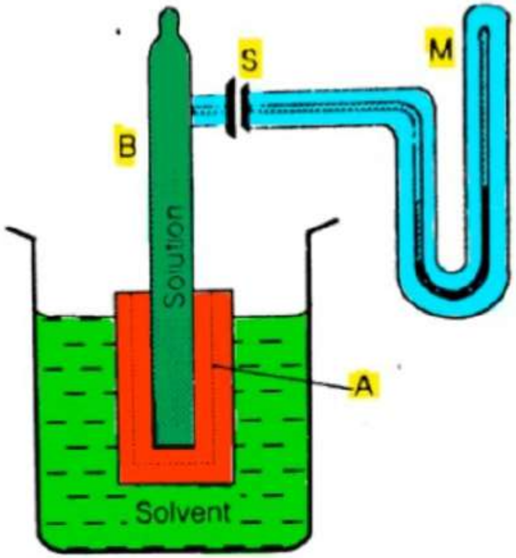




- In modern practice, electrical heating apparatus is used for a quick determination of melting points of camphor as also the mixture.
- The molal depression constant of pure camphor is 40°C. But since laboratory camphor may not be very pure, it is necessary to find the depression constant for a particular sample of camphor used.

→ Measurement of osmotic pressure :→

→ Pfeffer's method :→



- This method was developed by Pfeffer's in 1817 to measure osmotic pressure of solution.
- A porous pot (A) containing membrane of copper ferrocyanide in its wall is cemented to a glass tube (B) containing solution and attached to manometer (M).
- The porous pot is kept in pure solvent. The osmotic pressure exerted by the solution is given by the manometer.
- The method is of historical interest only and has been given up.

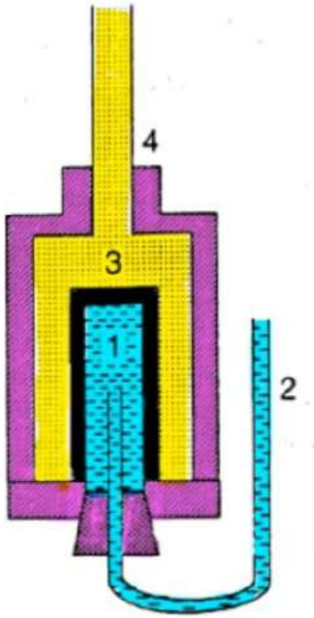
→ Disadvantage :→

- The osmotic pressure developed in dilute solution is very great and bursts the semi--permeable membrane used.
- It takes a long time to register the final osmotic pressure.

→ Measurement of osmotic pressure:→

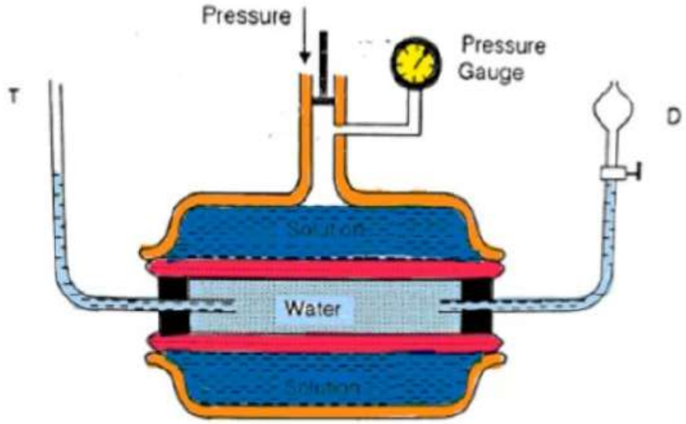
→ Morse and Frazer's method:→

- This method was developed by H.N. Morse, J.C.W. Frazer and their collaborators (1901-23).
- They preapared sophisticated semipermeable membranes of copper ferrocyanide by using an electric current. This made the membranes more tough and they were capable of withstanding high pressures without leakage.
- The apparatus has two chambers. Chamber 1 which has the semipermeable membrane deposited on its walls is fitted with water. Tube 2 also filled with water. Chamber 3 is filled with solution. When osmosis begins, solvent flow from 1 to 3 increasing the hydrostatic pressure in vessel 3. This hydrostatic pressure developed, which is equal to osmotic pressure, is measured by a manometer attached to 4.



→ Measurement of osmotic pressure:→

→ Berkley and Hartley's method (1909):→



- This is most simple, rapid and accurate method of measuring osmotic pressure. It is based on the fact that counter pressure applied on the solution so as to prevent osmosis is a measure of osmotic pressure.
- The apparatus consists of two concentric tubes, the inner one being that of porcelain having electrically deposited semi-permeable membrane of copper ferrocyanide in it's walls. The two ends of the inner tube are connected to a capillary T on one side and dropping funnel D on the other. The outer tube is made of gun metal and is fitted with arrangement for applying definite pressure.
- In the annular space between the tubes is introduced the solution whose osmotic pressure is to be measured while the inner tube is filled with water by means of dropping funnel up to a definite level T in the capillary tube.
- Due to osmosis the water from the inner tube tends to pass into the solution which is indicated by the downward motion of the water menisus in the capillary tube T. The external pressure is applied on the solution to prevent the flow of water and consequently lowering the meniscus. This pressure so applied is equal to osmotic pressure and is directly measured by means of pressure gauge attached to a piston.

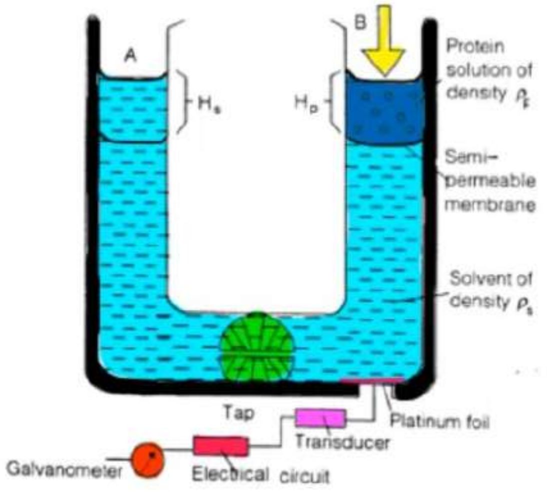
→ Advantages:→

(i) less time required (ii) Due to less stress there is no chance of SPM burst.

(iii) Strength of solution does not change during measurement and hence is more accurate.

→ Measurement of osmotic pressure :→

→ Electronic osmometer :→



- An osmometer adapted for rapid measurement of osmotic pressure using small volumes of sample was designed by Row and Abrams in 1907.
- The U-tube has a semi-peameable membrane arranged in it arm B which holds the protein solution (sample) above it while the solution lies beneath it.
- Arm 'A' also contains the same solvent.
- In the horizontal portion of the tube lies a very thin platinum foil which is connected further to a mechno-electronic transducer in a circuit with a galvanometer.
- A controlled air pressure is continuously exerted on the protein solution.
- When tap is closed, the system if not in equilibrium, tries to attain it. The solvent passes througth the membrane and the resulting pressure changes displaces the platinum foil. This is indicated on the galvanometer scale.
- If the system is in equilibrium, no deflection can be observed in the galvanometer.
- The osmotic pressure can be calculated by the following formula–

$$\boxed{\text{Osmotic pressure} = P + H_p\rho_p - H_s\rho_s - H_t}$$

where. P = Pressure applied to protein solution
H_p = Hight of column of protein above membrane
H_s = Hight of column of solvent above membrane
H_t = Effect due to difference in surface tension b/w protein solution and solvent
ρ_p & ρ_s = density of protein solution and solvent.

→ Reverse Osmosis :→

- Consider a solution separated from the pure solvent by a semipermeable membrane. If the pressure applied on the solution is more than the osmotic pressure, the solvent will start flowing from the solution towards the pure solvent. This phenomenon is known as reverse osmosis.
- Reverse osmosis (RO) technique is used for getting drinking water from the sea water, particularly in Gulf countries.
- The sea water is pumped into pressure vessel fitted with a suitable semipermeable membrane (SPM). Under the influence of high pressure, water from sea water passes out through the semipearmeable membrane.
- The rate of flow of water (Q_w) through the SPM is given by -

$$\boxed{Q_w = \frac{(\Delta P - \Delta \pi)\, K_w A}{\delta}}$$

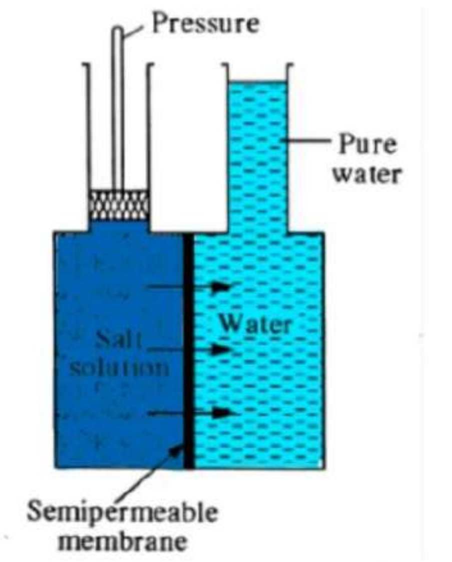
Where ΔP = hydraulic pressure differential across the membrane

$\Delta \pi$ = osmotic pressure differential across the membrane

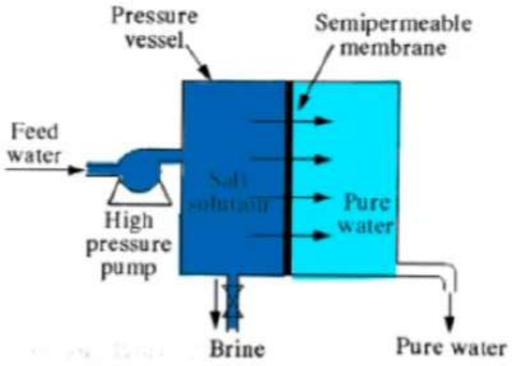
K_w = membrane peameability coefficient water

A = membrane area

δ = membrane thickness



Reverse Osmosis



RO Technique

→ Abnormal molar mass:→

- When the molecular mass determined by any of the colligative properties comes out to be different than the theoritically expected value then the substance is said to show abnormal molecular mass.
- Since colligative properties depend upon the number of particles (molecules or ions) of the solute in some cases where the solute associates or dissociates in solution, abnormal results are obtained.

1. Association:→

- There are many organic solutes which in non-aqueous solution undergo association, i.e. two or more molecules of the solute associate to form a bigger molecule. Thus, the number of effective molecules or particles decreases and, consequently, the colligative properties are less than that calculated on the basis of single molecules.
- Examples (1) Acetic acid in benzene
  (2) Chloroacetic acid in napthalene

In such cases, molecular masses of solutes will be higher than the true molar masses as indicated by their formulae.

Thus, the molar mass of acetic acid (CH_3COOH), in benzene, as determined from freezing point depression is, 118 instead of 60. It appears, therefore, that molecules of acetic acid exist largely as $(CH_3COOH)_2$ when dissolved in benzene.

2. Dissociation:→

- Inorganic acids, bases and salts in aqueous solution undergo dissociation, that is, the molecule break down into positively and negatively charged ions.

- In such cases, the number of effective particles increases and therefore colligative properties are much higher than those calculated on the basis of undissociated single molecules.

Example :- In case of KCl, in the aqueous solution, each molecule dissociates to give two ions.

$$KCl \rightarrow K^+ + Cl^-$$

Thus the number of particles becomes double, the observed value of colligative property is double than expected value and molar mass is half of the expected value.

→ van't Hoff factor:→

- In 1880, van't Hoff introduced a factor i, known as van't Hoff factor.
- This factor explains the extent of association or dissociation.

$$i = \frac{\text{Observed osmotic effect}}{\text{Normal osmotic effect}}$$

osmotic effect means colligative properties such as osmotic pressure, vapour pressure lowering, boiling point elevation and freezing point depression.

since colligative properties are inversaly proportional to molar mass of solute, it follows that

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Total number of moles of particles before association/dissociation}}$$

- In case of association, $i < 1$, e.g → Value for acetic acid in benzene = 0.5
- In case of dissociation, $i > 1$, e.g. → Value for KCl solution = 2
- Inclusion of van't Hoff factor modifies the equation for colligative properties as follows-

(i) Relative lowering of vapour pressure $\frac{p_1^0 - p_1}{p_1^0} = i \cdot \frac{n_2}{n_1}$

(ii) Elevation of boiling point $\Delta T_b = i k_b m$

(iii) Depression of freezing point $\Delta T_f = i k_f m$

(iv) osmotic pressure of solution $P = i \frac{n_2}{V} ST$

* Colligative properties are applicable for non-electrolyte which do not undergo association/dissociation.

→ Degree of dissociation and association of solute :→

1. Degree of dissociation :→

- By degree of dissociation is meant the fraction of the total number of molecule which dissociate, i.e. break into simpler molecules or ions.
- Consider one mole of uni-univalent electrolyte like potassium chloride dissolved in a given volume of water.

Let, α be its degree of dissociation. Then the number of moles of KCl left undissociated will be $1-\alpha$. At the same time, α moles of K^+ ions and α moles of Cl^- ions will be produced, as shown below –

$$\begin{array}{cccc} KCl & \rightleftharpoons & K^+ & + \; Cl^- \\ 1-\alpha & & \alpha & \alpha \end{array}$$

Thus total number of moles after dissociation $= 1-\alpha+\alpha+\alpha = 1+\alpha$

$$\text{Hence} \quad i = \frac{\text{Observed osmotic effect}}{\text{Normal osmotic effect}} = \frac{1+\alpha}{1}$$

Since colligative properties are inversely proportional to the molar mass of solute, therefore, Van't Hoff factor is given by -

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{1+\alpha}{1}$$

- Knowing the observed molar mass, the degree of dissociation, α can be easily calculated.

- **Example:-** Normal molar mass of KCl $= 74.5\ g\ mol^{-1}$

  observed molar mass (from freezing point depression) of KCl $= 38.75\ g\ mol^{-1}$

$$\frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{1+\alpha}{1}$$

$$\frac{74.5\ g\ mol^{-1}}{38.75\ g\ mol^{-1}} = 1+\alpha$$

or $1.923 = 1+\alpha$

or $\alpha = 1.923 - 1 = 0.923$

2. Degree of association:→

- By degree of association is meant the fraction of the total number of molecules which combine to form bigger molecules.
- Consider one mole of a solute dissolved in a given volume of a solvent.

  Suppose n simple molecule combine to form an associated molecule, i.e.

$$nA \rightleftharpoons (A)_n$$

Let, α be the degree of association. Then,

The number of unassociated moles $= 1-\alpha$

The number of associated moles $= \alpha/n$

$\therefore$ The number of effective moles $= 1-\alpha+\alpha/n$

Hence $$i = \frac{\text{Observed osmotic effect}}{\text{Normal osmotic effect}} = \frac{1-\alpha+\alpha/n}{1}$$

Since colligative properties are inversely proportional to the molar mass of solute. therefore, Van't Hoff factor is given by -

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{1-\alpha+\alpha/n}{1}$$

Thus by knowing n and the observed molar mass, the degree of association can be calculated.

- Example:- Since acetic acid associates to form dimer, hence

No. of moles before association → 1 $\quad$ 0

$$2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

No. of moles after association → $1-\alpha$ $\quad$ $\alpha/2$

The number of unassociated moles = $1-\alpha$ and the number of associated moles = $\alpha/2$

∴ The number of effective moles = $1-\alpha+\alpha/2$

Normal molar mass of acetic acid = $60\ g\ mol^{-1}$ and observed molar mass (from boiling point elevation is $117.8\ g\ mol^{-1}$

$$\frac{60\ g\ mol^{-1}}{117.8\ g\ mol^{-1}} = 1-\alpha+\alpha/2$$

$$\frac{60\ \text{g mol}^{-1}}{117.8\ \text{g mol}^{-1}} = 1-\alpha+\alpha/2$$

$$0.510 = 1-\alpha+\alpha/2$$

$$\alpha-\alpha/2 = 1-0.510$$

$$\alpha\left(1-\frac{1}{2}\right) = 1-0.510$$

$$\alpha\left(\frac{1}{2}\right) = 0.49$$

$$\alpha = 0.49\times 2$$

$$\alpha = 0.98$$