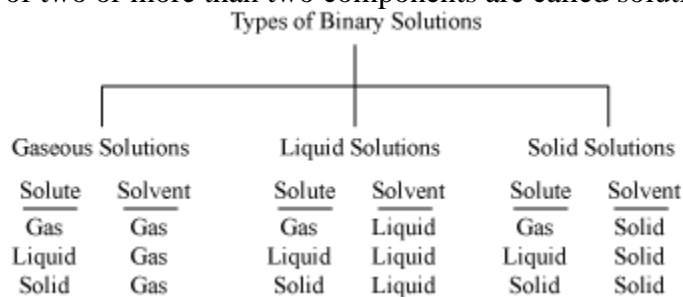


Solutions

Types of Solutions & Expressing Concentration of Solutions

Types of Solutions

- Homogeneous mixtures of two or more than two components are called solutions.



Expressing Concentration of Solutions

- Mass percentage (w/w)

$$\text{Mass \% of a component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100\%$$

- Volume percentage (v/v)

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100\%$$

- Mass by volume percentage (w/v)

$$\text{Mass by volume \%} = \frac{\text{Mass of the solute}}{\text{Total volume of solution}} \times 100\%$$

- Parts per million (ppm)

$$\text{Parts per million} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all the components of the solution}} \times 10^6$$

- Mole fraction (x)

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

For solution containing i number of components,

$$x_i = \frac{n_i}{n_1 + n_2 + n_3 + \dots + n_i} = \frac{n_i}{\sum n_i}$$

And, $x_1 + x_2 + x_3 + \dots + x_i = 1$

- Molarity (M)

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

- Molality (m)

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

Solubility

- Solubility of a substance is the maximum amount of the substance that can be dissolved in a specified amount of a solvent at a given temperature.
- Factors on which solubility depends:
 - Nature of solute and solvent
 - Temperature
 - Pressure

Solubility of a Solid in a Liquid

When a solute is dissolved in a solvent, the following dynamic equilibrium is established.



This equilibrium follows Le Chatelier's Principle.

- Effect of temperature:

According to Le Chatelier's principle, in a nearly saturated solution, if the dissolution process is –

 - Endothermic ($\Delta_{\text{sol}}H > 0$), then the solubility will increase with the increase in temperature
 - Exothermic ($\Delta_{\text{sol}}H < 0$), then the solubility will decrease with the increase in temperature
- Effect of pressure:
 - Pressure has no significant effect on the solubility of solids in liquids.
 - Reason – Solids and liquids are negligibly affected by pressure as they are highly incompressible.

Solubility of a Gas in a Liquid

- The solubility of gases in liquids increases with the increase in pressure.
 - Henry's law – The solubility of a gas in a liquid is directly proportional to the pressure of the gas.

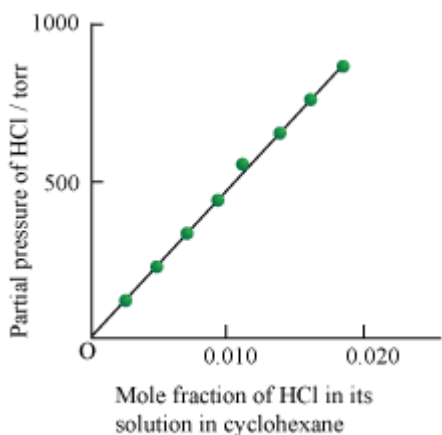
Or

The partial pressure of a gas in vapour phase (p) is directly proportional to the mole fraction of the gas (x) in the solution, i.e.,

$$p = K_H x$$

Where, K_H = Henry's law constant

The plot of the partial pressure of HCl vs. its mole fraction in a solution of cyclohexane is given below.



- Some important applications of Henry's law

(i) Bottles are sealed under high pressure to increase the solubility of CO_2 in soft drinks and soda water.

(ii) Henry's law states that the solubility of gas increases with an increase in pressure. Therefore, when a scuba diver dives into the sea, the increased sea pressure causes the nitrogen present in air to dissolve in his blood in great amounts. As a result, when he comes back to the surface, the solubility of nitrogen again decreases and the dissolved gas is released, leading to the formation of nitrogen bubbles in the blood. This results in the blockage of capillaries and leads to a medical condition known as 'bends', which are painful and dangerous to life. Hence, the oxygen tanks used by scuba divers are filled with air and diluted with helium to avoid bends.

(iii) The concentration of oxygen is low in the blood and tissues of climbers or people living at high altitudes. This is because at high altitudes, the partial pressure of oxygen is less than that at ground level. Low blood oxygen causes climbers to become weak and prevents them from thinking clearly. These are symptoms of 'anoxia'.

- Effect of temperature
Solubility of gases in liquids decreases with the increase in temperature.

Vapour Pressure of Liquid Solutions

- Let p_1, p_2 = Partial vapour pressure of two volatile components 1 and 2 of a mixture

$$P_1^0, P_2^0 = \text{Vapour pressure of pure components 1 and 2}$$

$$x_1, x_2 = \text{Mole fractions of the components 1 and 2}$$

$$p_{\text{total}} = \text{Total vapour pressure of the mixture}$$

Raoult's law

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

That is, for component 1,

$$p_1 \propto p_2$$

$$\text{And, } p_1 = P_1^0 x_1$$

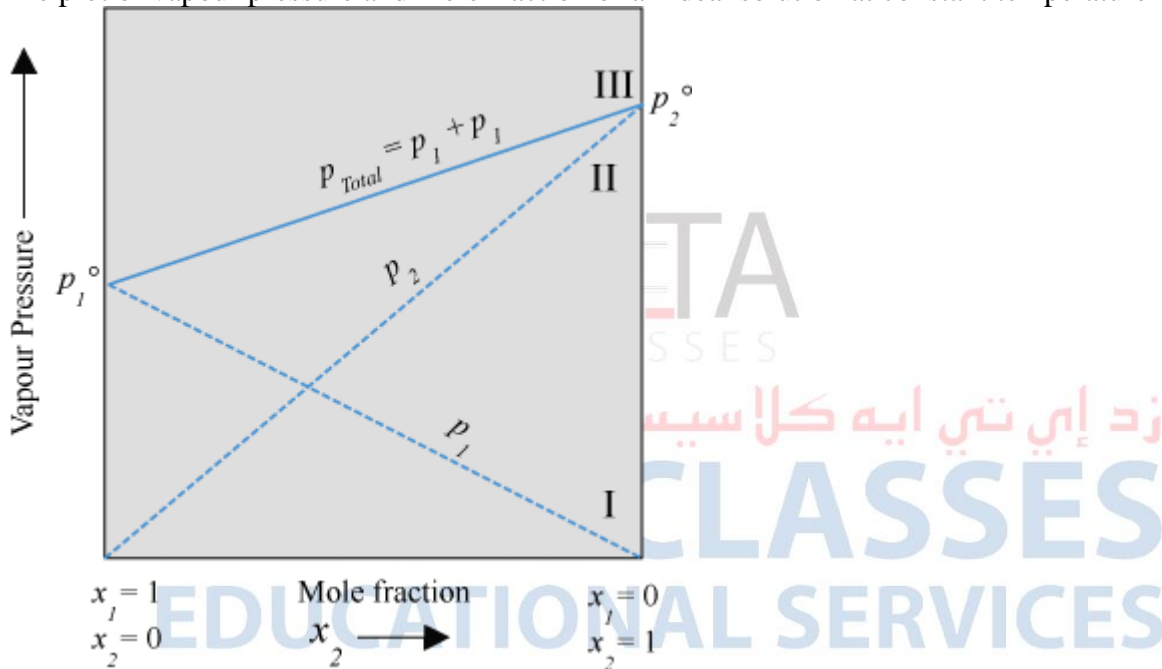
For component 2,

$$p_2 = P_2^0 x_2$$

According to Dalton's law of partial pressures,

$$\begin{aligned}
 P_{\text{total}} &= P_1 + P_2 \\
 &= P_1^0 x_1 + P_2^0 x_2 \\
 &= (1 - x_2) P_1^0 + x_2 P_2^0 \\
 P_{\text{total}} &= P_1^0 + (P_2^0 - P_1^0) x_2
 \end{aligned}$$

- From the above equation, it can be concluded that:
 - P_{total} can be related to mole fraction of any one component.
 - P_{total} varies linearly with x_2 .
 - Depending upon P_1^0 and P_2^0 , P_{total} increases or decreases with the increase of x_1 .
- The plot of vapour pressure and mole fraction of an ideal solution at constant temperature is shown below.



Here, maximum value of $P_{\text{total}} = P_2^0$

Minimum value of $P_{\text{total}} = P_1^0$

Here, $P_1^0 < P_2^0$ because it is assumed that component 1 is less volatile than component 2.

- The component of vapour phase in equilibrium with the solution is determined by the partial pressures of the components.
Let y_1, y_2 = Mole fractions of the components 1 and 2 respectively in the vapour phase

According to Dalton's law of partial pressures,

$$P_1 = y_1 P_{\text{total}}$$

$$P_2 = y_2 P_{\text{total}}$$

In general, we can write

$$P_i = y_i P_{\text{total}}$$

Raoult's Law as a Special Case of Henry's Law

- According to Raoult's law, the vapour pressure of a volatile component in a given solution is $P_i = y_i P_i^0$
- According to Henry's law, the partial vapour pressure of a gas (the component is so volatile that it exists as gas) in a liquid is
 $p = K_H x$
- It can be observed that in both the equations, the partial vapour pressure of the volatile component varies directly with its mole fraction. Only the proportionality constants K_H and P_i^0 are different. Thus, Raoult's law becomes a special case of Henry's law in which K_H is equal to P_i^0 .

Vapour Pressure of Solutions of Solids in Liquids

- When a non-volatile solute is added to a solvent, the vapour pressure of the liquid decreases.
 - Reason: The number of solvent molecules on the surface decreases and as a result, number of solvent molecules escaping from the surface decreases.
- Raoult's law in general form: For any solution, the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.
- Let us take a binary solution made by dissolving a non-volatile solute in a solvent. Since the solute is non-volatile, only the solvent molecules contribute to vapour pressure.

Let $P_1' =$ Vapour pressure of the solvent

$P_1^0 =$ Vapour pressure of the solvent in pure state

$x_1 =$ Mole fraction of the solvent

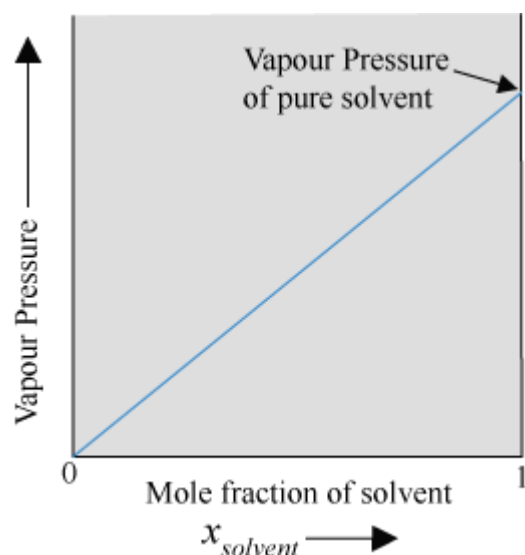
Then, according to Raoult's law,

$$p_1 = x_1'$$

$$\Rightarrow p_1 = x_1 \cdot P_1^0$$

Here, the proportionality constant is equal to the vapour pressure of the solvent in pure state.

The plot of vapour pressure vs. mole fraction of the solvent, which is linear, is shown below.



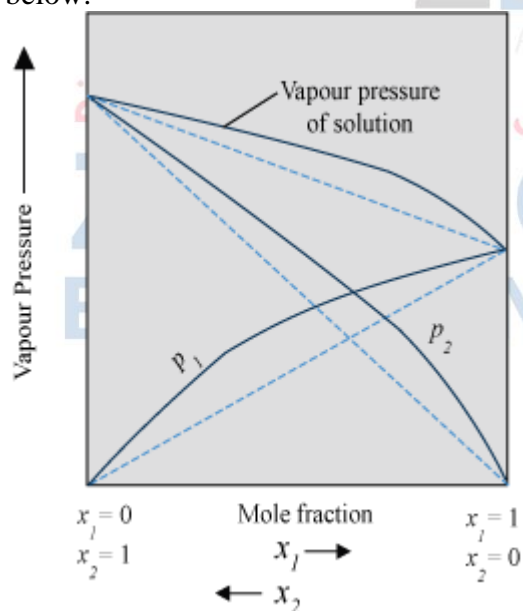
Ideal and Non-Ideal Solutions

Ideal Solution

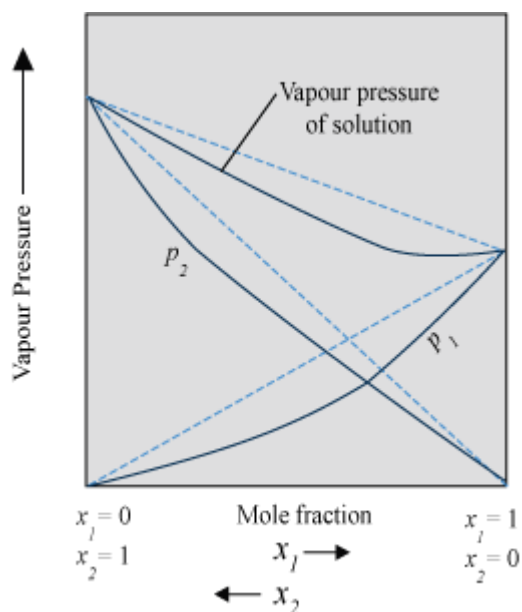
- Solutions which obey Raoult's law over the entire range of concentrations
- For ideal solution:
 - Enthalpy of mixing of the pure components to form the solution, $\Delta_{\text{mix}} H = 0$
 - Volume of mixing, $\Delta_{\text{mix}} V = 0$
- An ideal solution will be formed when intermolecular forces of attraction between the molecules of solute (A – A) and those between the molecules of solvent (B – B) are nearly equal to those between solute and solvent molecules (A – B).
 - Examples: *n*-Hexane and *n*-heptane, bromoethane and chloroethane, benzene and toluene

Non-Ideal Solutions

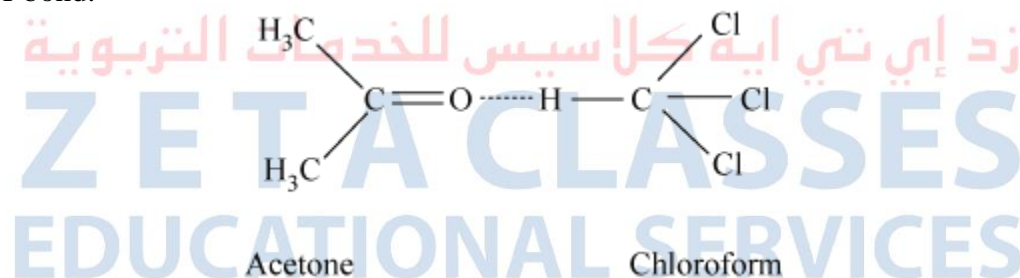
- Solutions which do not obey Raoult's law over the entire range of concentration
- The vapour pressure of a non-ideal solution is either higher or lower than that predicted by Raoult's law.
 - Positive deviation from Raoult's law – When vapour pressure is higher
 - Negative deviation from Raoult's law – When vapour pressure is lower
- Solution showing positive deviation from Raoult's law
 - The plot of vapour pressure of two component solutions as a function of mole fraction is shown below.



- The intermolecular forces of attraction between solute-solvent molecules are weaker than those between solute-solute molecules and solvent-solvent molecules. Therefore, solvent molecules can easily escape, resulting in increase in vapour pressure.
 - Example: Ethanol and acetone mixture
- Solution showing negative deviation from Raoult's law
 - The plot of vapour pressure of two component solutions as a function of mole fraction is shown below.



- The intermolecular forces of attraction between solute-solute molecules and solvent-solvent molecules are weaker than those between solute-solvent molecules. This results in the decreasing of vapour pressure.
- Example – Chloroform and acetone mixture
The intermolecular attractive forces between solute-solvent molecules increase due to the formation of H-bond.



Azeotropes

- Binary mixtures which have the same composition in liquid and vapour phase, and have constant boiling points
- Not possible to separate the components by fractional distillation
- Two types – Minimum boiling azeotrope

Maximum boiling azeotrope

- Minimum boiling azeotrope – Solution showing a large positive deviation from Raoult's law of specific composition
Example: Ethanol-water mixture containing ethanol approximately 95% by volume
- Maximum boiling azeotrope – Solution showing a large negative deviation from Raoult's law at specific composition
Example: Nitric acid-water mixture containing 68% nitric acid and 32% water by mass
The boiling point of this azeotrope is 393.5 K.

Colligative Properties and Determination of Molar mass

- Properties which depend upon the number of solute particles present in the solution irrespective of their nature, relative to the total number of particles present in the solution
- Examples: Relative lowering of vapour pressure of the solvent, depression of freezing point of the solvent, elevation of boiling point of the solvent, osmotic pressure of the solution

Relative Lowering of Vapour Pressure

- Relative lowering of vapour pressure is equal to the mole fraction of the solute.

$$\frac{p_1^0 - p_1}{p_1^0} = x_2$$

i.e.,

Where,

p_1^0 = Vapour pressure of the solvent

p_1 = Vapour pressure of the solution

x_2 = Mole fraction of the solute

$$x_2 = \frac{n_2}{n_1 + n_2}$$

However,

Where, n_2 = Number of moles of solute

n_1 = Number of moles of solvent

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

Now,

For dilute solution, $n_1 \gg n_2$

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1}$$

Therefore,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2}{M_2} \cdot \frac{M_1}{w_1}$$

Or,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

Or,

Where,

w_2 = Mass of solute

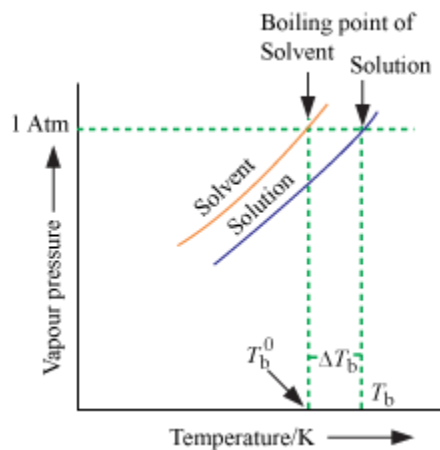
M_2 = Molar mass of solute

w_1 = Mass of solvent

M_1 = Molar mass of solvent

Elevation of Boiling Point

- With addition of non-volatile solute, vapour pressure decreases and hence, boiling point increases.



- Here, $\Delta T_b = T_b - T_b^0$ = Elevation of boiling point

Where,

T_b = Boiling of solution

T_b^0 = Boiling point of solvent

- $\Delta T_b \propto m$ (for dilute solution)

$\Rightarrow \Delta T_b = K_b m$

Where,

m = Molality

K_b = Proportionality constant known as Boiling Point Elevation Constant or Molal Elevation Constant or Ebullioscopic constant (Unit = K kg mol⁻¹)

$$m = \frac{\frac{w_2}{M_2}}{\frac{w_1}{1000}} = \frac{1000 \times w_2}{M_2 \times w_1}$$

However,

Where,

w_2 = Mass of solute

M_2 = Molar mass of solute

w_1 = Mass of solvent

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

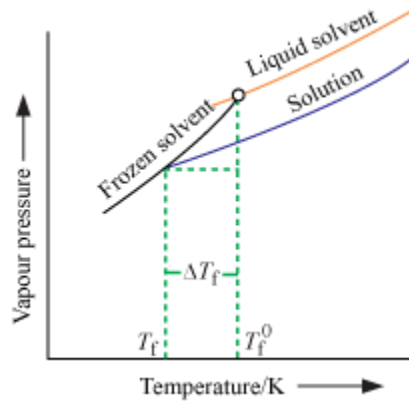
Now,

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

Or,

Depression of Freezing point

- With addition of non-volatile solute, vapour pressure decreases, which leads to a decrease in freezing point.



- Here, $\Delta T_f = T_f^0 - T_f =$ Depression of freezing point

Where,

T_f^0 = Freezing point of solvent

T_f = Freezing point of solution

- For dilute solution (ideal solution),

$\Delta T_f \propto m$

$\Rightarrow \Delta T_f = K_f m$

Where,

m = Molality

K_f = Proportionality constant known as Freezing Point Constant or Molal Depression Constant or Cryoscopic constant (Unit = $K \text{ kg mol}^{-1}$)

$$m = \frac{\frac{w_2}{M_2}}{\frac{w_1}{1000}} = \frac{1000 \times w_2}{M_2 \times w_1}$$

However,

Where,

w_2 = Mass of solute

M_2 = Molar mass of solute

w_1 = Mass of solvent

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

Now,

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

Or,

- The value of K_b and K_f can be determined by the following relations:

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{\text{vap}} H}$$

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{\text{fus}} H}$$

Where,

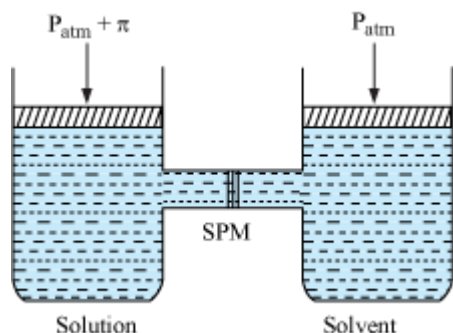
M_1 = Molar mass of the solvent

R = Gas constant

$\Delta_{\text{vap}} H$ = Enthalpy of vaporisation of the solvent $\Delta_{\text{fus}} H$ = Enthalpy of fusion of the solvent

Osmosis and Osmotic Pressure

- The process of flow of solvent molecules from pure solvent to solution or from solution of lower concentration to solution of higher concentration through a semi-permeable membrane is called osmosis.
- The pressure required to just stop the flow of solvent due to osmosis is called osmotic pressure (π) of the solution.
 - The osmotic pressure π has to be applied to the solution to prevent osmosis.



- For dilute solution, osmotic pressure is directly proportional to the molarity C of the solution at a given temperature T .

That is, $\pi = CRT$ (R = Gas constant)

$$\Rightarrow \pi = \left(\frac{n_2}{V} \right) RT$$

Where,

n_2 = Number of moles of solute

V = Volume of the solution in litres

Again,
$$n_2 = \frac{w_2}{M_2}$$

Where, w_2 = Mass of the solute

M_2 = Molar mass of the solute

$$\pi = \left(\frac{\frac{w_2}{M_2}}{V} \right) RT$$

Now,

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

Or,

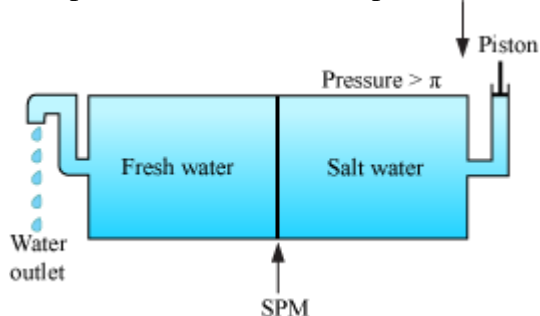
$$M_2 = \frac{w_2 RT}{\pi V}$$

Or,

- Now, osmosis occurs between two isotonic solutions.
 - Isotonic solutions – Solutions having same concentration of solute These solutions have same osmotic pressure.
 - Hypotonic solution – Solution having a low concentration of solute relative to another
 - Hypertonic solution – Solution having a high concentration of solute relative to another

Reverse Osmosis and Water purification

- If the pressure applied on the solution is greater than its osmotic pressure, then the direction of osmosis is reversed i.e., the solvent starts passing from solution to solvent. The phenomenon is called reverse osmosis.
 - This phenomenon is used in purification (desalination) of sea water.



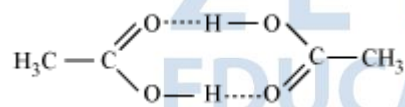
Abnormal Molar Masses

- Colligative property $\propto \frac{1}{\text{Molar mass of the solute}}$
- Therefore, due to association or dissociation of molecules, the molar mass of a substance calculated from its colligative property is either lower or higher than the expected or normal value. Such molar mass is called **abnormal molar mass**.

Dissociation:



Association:



- To account for the extent of dissociation or association, van't Hoff introduced a factor i , known as the van't Hoff factor.

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

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

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

- Value of i :

For association, $i < 1$

For dissociation, $i > 1$

No association or dissociation, $i = 1$

- Modified equations for colligative properties after inclusion of van't Hoff factor
- Relative lowering of vapour pressure of solvent,

$$\frac{p_1^0 - p_1}{p_1^0} = i \frac{n_2}{n_1}$$

- Elevation of boiling point, $\Delta T_b = iK_b m$
- Depression of freezing point, $\Delta T_f = iK_f m$
- Osmotic pressure of solution, $\pi = in_2RT/V$

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