## 2. SOLUTIONS

Solutions are homogeneous mixtures containing two or more components. Generally, the component that is present in larger quantity is called solvent. Solvent determines the physical state of the solution. One or more components present in the solution other than solvent are called solutes. [Or, the substance which is dissolved is called solute and the substance in which solute is dissolved is called solvent].

Solutions containing only two components are called binary solutions. Here each component may be solid, liquid or in gaseous state. Based on this, solutions are of the following types:

| Types of Solution | Solute | Solvent |  |
| :--- | :--- | :--- | :--- |
| Gaseous solutions | Gas | Gas | Mixture of $\mathrm{O}_{2}$ and $\mathrm{CO}_{2}$ |
|  | Liquid | Gas | Chloroform mixed with nitrogen gas, water-vapour in air |
|  | Solid | Gas | Camphor in nitrogen gas, naphthalene in air |
| Liquid solutions | Gas | Liquid | Oxygen dissolved in water, soda water |
|  | Liquid | Liquid | Alcohol dissolved in water, dilute acids and alkalies |
|  | Solid | Liquid | Salt in water, glucose in water |
| Solid solutions | Gas | Solid | Hydrogen in Pd, Pt, Ni etc |
|  | Liquid | Solid | Amalgam of mercury with sodium |
|  | Solid | Solid | Gold ornaments, alloys of metals |

## Concentration of Solutions

Composition of a solution can be expressed in terms of concentration. Concentration is defined as the number of moles of solute present per litre of the solution. The concentration of a solution can be expressed by several ways.
(i) Mass percentage $(\mathbf{w} / \mathbf{w})$ : The mass percentage of a component in a solution is defined as the mass of the component present in 100 parts by mass of the solution.
i.e. Mass \% of a component $=$ Mass of the component in the solution $\times 100$

Total mass of the solution
For e.g. $10 \%$ aqueous solution of glucose by mass means that 10 g of glucose is dissolved in 90 g of water resulting in a 100 g solution.
Concentration described by mass percentage is commonly used in industrial chemical applications.
(ii) Volume percentage ( $\mathbf{v} / \mathrm{v}$ ): The volume percentage is defined as the volume of a component present in 100 parts by volume of the solution.
i.e. Volume $\%$ of a component $=$ Volume of the component $\times 100$

Total volume of solution
For example, $10 \%$ ethanol solution in water means that 10 mL of ethanol is dissolved in 90 mL of water such that the total volume of the solution is 100 mL .
Concentration of solutions containing liquids is commonly expressed in this unit.
(iii) Mass by volume percentage ( $\mathbf{w} / \mathrm{v}$ ): It is the mass of solute dissolved in 100 mL of the solution It is commonly used in medicine and pharmacy.

Mass/volume \% of a component $=\frac{\text { Mass of the component in the solution } \times 100}{\text { Total }} 100$
Total volume of the solution
(iv) Parts per million (ppm): When a solute is present in trace quantities (i.e. very small amounts), its concentration is expressed in parts per million ( ppm ). It is defined as the number of parts of a particular component in million parts of the solution.

$$
\text { i.e. Parts per million }(\mathrm{ppm})=\frac{\text { Number of parts of the component } \times 10^{6}}{\text { Total number of parts of all the components of the solution }}
$$

Concentration in parts per million can be expressed as mass to mass, volume to volume and mass to volume. The concentration of pollutants in water or atmosphere is expressed in terms of $\mu \mathrm{g} \mathrm{m}^{-1}$ or ppm.
(v) Mole fraction ( $\mathbf{x}$ ): It is defined as the ratio of the number of moles of a particular component to the total number of moles of solution.
Mole fraction of a component $=$ Number of moles of the component

> Total number of moles of all the components

For example, in a binary solution, if the number of moles of $A$ and $B$ are $n_{A}$ and $n_{B}$ respectively, then the mole fraction of $A\left(x_{A}\right)=n_{A} /\left(n_{A}+n_{B}\right)$
and that of the component $B\left(x_{B}\right)=n_{B} /\left(n_{A}+n_{B}\right)$
$x_{A}+x_{B}=1$
i.e. in a given solution sum of the mole fractions of all the components is unity. If there are i components, then

$$
x_{1}+x_{2}+x_{3}+\ldots \ldots \ldots \ldots \ldots \ldots+x_{i}=1
$$

Mole fraction is useful in describing the calculations involving gas mixtures.
(vi) Molarity (M): It is defined as the number of moles of solute dissolved per litre of solution.
i.e. Molarity (M) $=\frac{\text { Number of moles of solute ( } \mathrm{n} \text { ) }}{\text { Volume of solution in litre (V) }}$
$\begin{aligned} & \text { Or, Molarity }(M)=\frac{\text { Mass of solute }}{\text { Molar mass of solute } \times \text { Volume of solution in } L} \\ & \text { Or, Molarity }(M)=\frac{\text { Mass of solute }\left(W_{B}\right) \times 1000}{\text { Molar mass of solute }\left(M_{B}\right) \times \text { Volume of solution in } \mathrm{mL}(\mathrm{V})}\end{aligned}$
For example, 0.25 M solution of NaOH means that 0.25 mol of NaOH is dissolved in one litre of solution.
(vii) Molality (m): It is defined as the number of moles of the solute present per kilogram (kg) of the solvent.
i.e. Molality $(m)=\frac{\text { Number of moles of solute(n) }}{\text { Mass of solvent in } \mathrm{kg}\left(W_{A}\right)}$

Or, Molality ( m ) = Mass of solute ( $\mathrm{W}_{\mathrm{B}}$ )
Molar mass of solute $\left(\mathrm{M}_{\mathrm{B}}\right) \times$ Volume of solution in $\mathrm{L}(\mathrm{V})$
Or, Molality $(m)=\frac{\text { Mass of solute }\left(W_{B}\right) \times 1000}{\text { Molar mass of solute }\left(\mathrm{M}_{B}\right) \times \text { Volume of solution in } \mathrm{mL}(\mathrm{V})}$
For example, 1 molal ( m ) solution of KCl means that $1 \mathrm{~mol}(74.5 \mathrm{~g})$ of KCl is dissolved in 1 kg of water.
(vii) Normality ( $\mathbf{N}$ ): It is defined as the no. of gram equivalents of solute present per litre of the solution.
i.e., Normality ( $N$ ) = Number of gram equivalents of solute

Volume of solution in litre
Or, Normality ( N ) =
Mass of solute
Equivalent mass of solute $\times$ Volume of solution in $L$
Or, Normality ( N ) = Mass of solute $\times 1000$
Equivalent mass of solute $x$ Volume of solution in mL
Among the different methods for expressing the concentration of solution, mass \%, ppm, mole fraction and molality are independent of temperature; whereas molarity, normality and volume $\%$ are depend on temperature. This is because volume depends on temperature and the mass does not.

## SOLUBILITY

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent. It depends upon the nature of solute and solvent, temperature and pressure.

## Solubility of a Solid in a Liquid

It is observed that polar solutes dissolve in polar solvents and non polar solutes in non polar solvents. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or the general principle related to solubility is that "like dissolves like".

## Saturated and Unsaturated solutions

A solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution. Here there is a dynamic equilibrium between the dissolved solute and the undissolved solute. A solution in which more solute can be dissolved at the same temperature is called an unsaturated solution.

## Effect of temperature

The solubility of a solid in a liquid mainly depends on temperature. Since the dissolution of a solid in a liquid is an equilibrium process, it should follow Le Chateliers Principle. In general, if in a nearly saturated solution, the dissolution process is endothermic ( $\Delta_{\text {sol }} H>0$ ), the solubility should increase with rise in temperature and if it is exothermic $\left(\Delta_{\text {sol }} H>0\right)$ the solubility should decrease with temperature.

## Effect of pressure

Since solids and liquids are highly incompressible, pressure does not have any significant effect on solubility of solids in liquids.

## Solubility of a Gas in a Liquid

Solubility of gases in liquids is greatly affected by pressure and temperature. The solubility of a gas increases with increase of pressure.

A quantitative relation between pressure and solubility of a gas in a liquid was first given by Henry, which is known as Henry's law. "The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas".

Or, "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas $(x)$ in the solution" and is expressed as:

$$
p=K_{H} x
$$

Here $K_{H}$ is the Henry's law constant. The value of $K_{H}$ depends on the nature of the gas and temperature. As the value of KH increases, the solubility of the gas in the liquid decreases.

A graph of partial pressure ( $p$ ) of the gas against mole fraction ( $x$ ) of the gas in solution is a straight line as follows. The slope of the graph gives the value of $\mathrm{K}_{\mathrm{H}}$.


As the temperature increases solubility of a gas in a liquid decreases. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

## Applications of Henry's law

1. To increase the solubility of $\mathrm{CO}_{2}$ in soft drinks and soda water, the bottle is sealed under high pressure.
2. Scuba divers carry oxygen cylinders to breath under deep sea. At high pressure under water, the solubility of atmospheric gases in blood increases. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends. To avoid bends the cylinders used by scuba divers are filled with air diluted with helium ( $11.7 \%$ helium, $56.2 \%$ nitrogen and $32.1 \%$ oxygen).
3. At high altitudes the partial pressure of oxygen 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 altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly. This condition is known as anoxia.

## Effect of Temperature

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved during this process. The dissolution process involves a dynamic equilibrium and thus follows Le-Chatelier's Principle. As dissolution is an exothermic process, the solubility should decrease with increase of temperature.

## Vapour Pressure of Liquid Solutions

In liquid solutions, the solvent is always a liquid. The solute can be a gas, a liquid or a solid. Generally, the liquid solvent is volatile. The solute may or may not be volatile. Based on the volatility of solute, the vapour pressure of the solution is greater or less than that of the solvent.

## Vapour Pressure of Liquid-Liquid Solutions - Raoult's Law

A quantitative relationship between the vapour pressure and mole fraction of solute in a solution was first given by a French chemist F.M Raoult and it is known as Raoult's Law. It states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

Consider a binary solution of two volatile liquids 1 and 2 . Let $p_{1}$ and $p_{2}$ be the partial vapour pressures of the two components 1 and 2 respectively and $p_{\text {total }}$ be the total vapour pressure. Let $x_{1}$ and $x_{2}$ be the mole fractions of the two components 1 and 2 respectively.

Then according to Raoult's law,
for component 1, $\mathrm{p}_{1} \propto \mathrm{x}_{1}$
or, $p_{1}=p_{1}{ }^{0} x_{1}$
and for component $2, \mathrm{p}_{2} \propto \mathrm{x}_{2}$
or, $p_{2}=p_{2}{ }^{0} x_{2}$
Where $p_{1}{ }^{0}$ and $p_{2}{ }^{0}$ are the vapour pressures of the pure components $1 \& 2$ respectively.
According to Dalton's law of partial pressures, the total pressure ( $\mathrm{p}_{\text {total }}$ ) will be the sum of the partial pressures of the components of the solution.

So, $p_{\text {total }}=p_{1}+p_{2}$
Substituting the values of $p_{1}$ and $p_{2}$, we get

$$
\begin{aligned}
p_{\text {total }} & =x_{1} p_{1}{ }^{0}+x_{2} p_{2}{ }^{0} \\
& =\left(1-x_{2}\right) p_{1}^{0}+x_{2} p_{2}^{0} \\
\text { Or, } p_{\text {total }} & =p_{1}{ }^{0}+\left(p_{2}{ }^{0}-p_{1}^{0}\right) x_{2}
\end{aligned}
$$

Plots of $p_{1}$ or $p_{2}$ against the mole fractions $x_{1}$ and $x_{2}$ give straight lines (I and II). Similarly the plot of $p_{\text {total }}$ versus $x_{2}$ (line III) is also linear.


The composition of vapour phase in equilibrium with the solution is determined from the partial pressures of the components. If $y_{1}$ and $y_{2}$ are the mole fractions of the components 1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressures:

$$
\begin{aligned}
& p_{1}=y_{1} p_{\text {total }} \text { and } p_{2}=y_{2} p_{\text {total }} \\
& \text { In general, } p_{i}=y_{i} p_{\text {total }}
\end{aligned}
$$

## 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 solution is given by $p_{i}=x_{i} p_{i}$. According to Henry's law, solubility of a gas in a liquid is given by $p=K_{H} x$.

If we compare the equations for Raoult's law and Henry's law, we can see that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. Only the proportionality constant $K_{H}$ differs from $p_{1}{ }^{0}$. Thus, Raoult's law becomes a special case of Henry's law in which $K_{H}$ becomes equal to $\mathrm{p}_{1}{ }^{0}$.

## Vapour Pressure of Solutions of Solids in Liquids

The vapour pressure of a liquid is the pressure exerted by the vapour in equilibrium with its own liquid. If a non-volatile solute is added to a pure solvent, the vapour pressure of the resulting solution is always lower than that of the pure solvent. This is because in a pure solvent, there are only solvent molecules, which can vapourise. But when a non-volatile solute is added to the solvent, a fraction of the surface is occupied by solute molecules. So the number of solute molecules passing to the vapour phase decreases and hence the vapour pressure also decreases. The decrease in the vapour pressure of solvent depends on the quantity of non-volatile solute present in the solution and not on its nature. For such a solution the Raoult's law can be stated as, for any solution, the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.

Consider a binary solution containing a solvent 1 and solute 2 . Since the solute is non-volatile, only the solvent molecules are present in vapour phase and contribute to vapour pressure.

Let $p_{1}$ be the vapour pressure of the solvent, $x_{1}$ be its mole fraction, $p_{1}{ }^{0}$ be its vapour pressure in the pure state. Then according to

Raoult's law, $\mathrm{p}_{1} \propto \mathrm{x}_{1}$

$$
\text { or, } \mathrm{p}_{1}=\mathrm{p}_{1}{ }^{0} \mathrm{x}_{1}
$$

A graph between the vapour pressure and the mole fraction of the solvent is linear as follows:


## Ideal and non-ideal solutions

Liquid - liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.

1. Ideal solutions:

These are solutions which obey Raoult's law over the entire range of concentration. For such solutions, the enthalpy of mixing ( $\Delta \mathrm{H}_{\text {mix }}$ ) of the pure components is zero and also volume of mixing $\left(\Delta \mathrm{V}_{\text {mix }}\right)$ is zero. i.e. for an ideal solution,

$$
\mathrm{P}_{1}=\mathrm{P}_{1}^{0} \mathrm{X}_{1}, \mathrm{P}_{2}=\mathrm{P}_{2}^{0} \mathrm{X}_{2}, \Delta \mathrm{H}_{\text {mix }}=0 \text { and } \Delta \mathrm{V}_{\text {mix }}=0
$$

Ideal behaviour can be explained by considering two components $A$ and $B$. In pure components, the inter molecular attractive interactions will be of types $A-A$ and $B-B$. In solution, in addition to these two interactions, $A-B$ type of interaction will also be present. If the $A-A$ and $B-B$ interactions are nearly equal to the A-B interaction, the solution behaves ideally. i.e. solute-solute interactions and solvent-solvent interactions are nearly equal to solute-solvent interaction.
A perfectly ideal solution is rare. But some solutions are nearly ideal in behaviour.
E.g. solutions of $n$-hexane and $n$-heptane, bromoethane and chloroethane, benzene and toluene etc.

## 2. Non-ideal solutions:

These are solutions which do not obey Raoult's law over the entire range of concentration. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law. If it is higher, the solution exhibits positive deviation and if it is lower, it exhibits negative deviation from Raoult's law. The plots of vapour pressure against mole fractions for such solutions are as follows:



In the case of positive deviation from Raoult's law, A-B interactions are weaker than A-A and B-B interactions. i.e., in this case solute-solvent interactions are weaker than solute-solute and solvent-solvent
interactions. So more molecules are escaped to vapour phase and hence the vapour pressure of the solution increases.
E.g. solutions of ethanol and acetone, acetone and $\mathrm{CS}_{2}$, acetone and $\mathrm{CCl}_{4}$ etc.

In case of negative deviation from Raoult's law, the A-B interactions are stronger than A-A and B-B interactions. i.e. solute-solvent interactions are stronger than solute-solute interaction and solvent-solvent interaction. So number of molecules escaped to vapour phase decreases and hence the vapour pressure of the solution decreases.
E.g. solution of phenol and aniline, chloroform and acetone etc.

## Azeotropes

They are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. For such solutions, it is not possible to separate the components by fractional distillation. There are two types of azeotropes: minimum boiling azeotrope and maximum boiling azeotrope.

The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a particular composition. E.g. 95\% ethanol solution by volume.

The solutions which show large negative deviation from Raoult's law form maximum boiling azeotrope at a particular composition. E.g. a mixture of $68 \%$ Nitric acid and $32 \%$ water by mass forms a maximum boiling azeotrope at 393.5 K .

## COLLIGATIVE PROPERTIES AND DETERMINATION OF MOLARMASS

The properties which depend only on the number of solute particles and not on their nature are called Colligative properties. The important colligative properties are: Relative lowering of Vapour pressure, Elevation of Boiling point, Depression of Freezing point and Osmotic Pressure.

## 1. Relative lowering of Vapour Pressure

When a non-volatile solute is added to a pure solvent, the vapour pressure (V.P) of the resulting solution is lower than that of the pure solvent. The difference between the vapour pressure of pure solvent and that of the solution is called lowering of vapour pressure ( $\Delta \mathrm{P}$ ).

Consider a binary solution containing a non-volatile solute 2 dissolved in a solvent 1. Let $P_{1}{ }^{0}$ be the vapour pressure of pure solvent 1 and $P_{1}$ be the vapour pressure of solution. Then according to Raoult's law, $\mathrm{P}_{1}=\mathrm{P}_{1}{ }^{0} \mathrm{X}_{1}$
The lowering of vapour pressure of the solvent $(\Delta P)=P_{1}{ }^{0}-P_{1}$

$$
=P_{1}^{0}-P_{1}{ }^{0} X_{1}
$$

$$
\text { Or, } \quad \Delta P=P_{1}^{0}\left(1-x_{1}\right)
$$

But $x_{1}+x_{2}=1$. Therefore $1-x_{1}=x_{2}$
So $\Delta P=P_{1}{ }^{0} \cdot x_{2}$
Or, $\frac{\Delta P}{P_{1}{ }^{0}}=x_{2}$, the mole fraction of the solute.
Where $\Delta \mathrm{P} / \mathrm{P}_{1}{ }^{0}$ is called relative lowering of vapour pressure. It is defined as the ratio of the lowering of vapour pressure to the vapour pressure pure solvent.

But $x_{2}=\frac{n_{2}}{n_{1}+n_{2}}$
Where $n_{1}$ and $n_{2}$ are the number of moles of solvent and solute respectively.
For dilute solutions, $n_{2} \ll n_{1}$ and hence $n_{2}$ in the denominator can be neglected.
So, $x_{2}=n_{2} / n_{1}$
Therefore, $\frac{\Delta \mathrm{P}}{\mathrm{P}_{1}{ }^{0}}=\frac{\mathrm{n}_{2}}{\mathrm{n}_{1}}$

$$
\begin{array}{ll}
\text { Or, } & \frac{\Delta \mathrm{P}}{\mathrm{P}_{1}{ }^{0}=\mathrm{w}_{2} / \mathrm{M}_{2}} \mathrm{~W}_{1} / \mathrm{M}_{1} \\
\text { Or, } & \frac{\Delta \mathrm{P}}{\mathrm{P}_{1}}=\frac{\mathrm{W}_{2} \times \mathrm{M}_{1}}{\mathrm{~W}_{1} \times \mathrm{M}_{2}}
\end{array}
$$

Where $\mathrm{w}_{1}$ and $\mathrm{w}_{2}$ are the masses and $\mathrm{M}_{1}$ and $\mathrm{M}_{2}$ are the molar masses of solvent and solute respectively.

## 2. Elevation of Boiling Point ( $\Delta T_{b}$ )

Boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure.

When a non-volatile solute is added to a pure solvent, the boiling point of the resulting solution is always greater than that of the pure solvent. The difference between the boiling point of solution $\left(\Delta T_{b}\right)$ and that of the pure solvent $\left(T_{b}{ }^{0}\right)$ is called elevation of boiling point $\left(T_{b}\right)$.
i.e. $\Delta T_{b}=$ Boiling point of solution - Boiling point of pure solvent

Or, $\Delta T_{b}=T_{b}-T_{b}{ }^{0}$
If we plot a graph between the vapour pressure and temperature, we get the following graphs for the pure solvent and the solution.

Boiling point of


For dilute solutions, the elevation of boiling point is directly proportional to molality (m).
i.e. $\Delta T_{b} \propto m$
or, $\Delta T_{b}=K_{b} . m$
Where $\mathrm{K}_{\mathrm{b}}$ is a constant called Boiling Point Elevation Constant or Molal Elevation Constant or Ebullioscopic Constant. It is defined as the elevation of boiling point for 1 molal solution.
The unit of $K_{b}$ is $\mathrm{K} \mathrm{kg} / \mathrm{mol}$. For water, $\mathrm{K}_{\mathrm{b}}=0.52 \mathrm{~K} \mathrm{~kg} / \mathrm{mol}$.
But molality $m=\frac{w_{2} \times 1000}{M_{2} \times w_{1}}$
Therefore, $\Delta T_{b}=\frac{K_{b} \cdot W_{2} \times 1000}{\mathrm{M}_{2} \cdot \mathrm{~W}_{1}}$
Or, $\quad \Delta \mathrm{T}_{\mathrm{b}}=\frac{1000 \mathrm{~K}_{\mathrm{b}} \cdot \mathrm{W}_{2}}{\mathrm{w}_{1} \cdot \mathrm{M}_{2}}$
Where $\mathrm{w}_{1}=$ mass of solvent, $\mathrm{w}_{2}=$ mass of solute, $\mathrm{M}_{2}=$ molar mass of solute. By using this equation, we can calculate the molar mass of unknown solute.
3. Depression of Freezing point ( $\Delta T_{f}$ )

Freezing point is the temperature at which the solid phase and liquid phase of a substance has the same vapour pressure.

According to Raoult's law, when a non-volatile solute is added to a pure solvent, its vapour pressure decreases. Now it would become equal to that of solid solvent at lower temperature. Thus the freezing point of the solvent decreases. The difference between the freezing point (f.p) of pure solvent ( $T_{f}{ }^{0}$ )and that of the solution $\left(T_{f}\right)$ is called depression of freezing point $\left(\Delta T_{f}\right)$.
i.e. $\Delta T_{f}=T_{f}^{0}-T_{f}$

The vapour pressure - temperature graph representing the freezing point of pure solvent and solution is as follows:


For dilute solutions, it is found that the depression of freezing point $\left(\Delta T_{f}\right)$ is directly proportional to molality ( m ) of the solution.

Thus $\Delta \mathrm{T}_{\mathrm{f}} \propto \mathrm{m}$
Or, $\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{K}_{\mathrm{f}} \cdot \mathrm{m}$
Where $K_{f}$ is a constant called Freezing Point Depression Constant or Molal Depression Constant or Cryoscopic Constant. It is defined as the depression of freezing point for 1 molal solution. The unit of $\mathrm{K}_{\mathrm{f}}$ is K $\mathrm{kg} / \mathrm{mol}$. For water, $\mathrm{K}_{\mathrm{f}}=1.86 \mathrm{~K} \mathrm{~kg} / \mathrm{mol}$.

We know that molality $m=w_{2} \times 1000$
Therefore, $\Delta T_{f}=K_{f} . W_{2} \times 1000$

$$
\text { Or, } \quad \Delta \mathrm{T}_{\mathrm{f}}=\frac{1000 \mathrm{~K}_{\mathrm{f}} \cdot \mathrm{~W}_{2}}{\mathrm{w}_{1} \cdot \mathrm{M}_{2}}
$$

## 4. Osmosis and Osmotic Pressure

Osmosis is the process of flow of solvent molecules from pure solvent to solution through a semi-
permeable membrane. Or, it is the flow of solvent molecules from lower concentration side to a higher concentration side through a semi-permeable membrane (SPM).

A membrane that allows the passage of solvent molecules only is called a semi-permeable membrane. E.g. egg membrane, all animal and plant membrane. Cellulose acetate is an example for artificial SPM.

Osmotic pressure is defined as the excess pressure that must be applied on solution side to stop
osmosis. Or, it is the pressure that just stops the flow of solvent molecules. It is denoted by $\pi$. It is a colligative property, since it depends on the number of solute molecules and not on their nature. For dilute solutions, osmotic pressure is proportional to the molarity (C) and temperature ( T ).
i.e. $\pi=$ CRT

Here $R$ is the universal gas constant. ( $R=0.0821 \mathrm{Latm} / \mathrm{K} / \mathrm{mol}$ or $R=0.083 \mathrm{Lbar} / \mathrm{K} / \mathrm{mol}$ ).
But $C=n_{2} / V$, the concentration of the solution.
Therefore, $\pi=\mathrm{n}_{2}$. RT

$$
\begin{aligned}
& \text { Or, } \pi V=n_{2} R T \\
& \text { Or, } \pi V=\frac{w_{2} R T}{M_{2}}
\end{aligned}
$$

Where V is the volume of the solution, $\mathrm{w}_{2}$ is the mass of solute and $\mathrm{M}_{2}$ is the molar mass of solute.
Thus by knowing all other values, we can calculate the molar mass of the unknown solute by the equation:
$M_{2}=\frac{w_{2} R T}{\pi V}$
Advantages of osmotic pressure measurement over other colligative property measurement

1. Osmotic pressure measurement can be done at room temperature.
2. Here molarity of the solution is used instead of molality, which can be determined easily.
3. The magnitude of osmotic pressure is large even for very dilute solutions.
4. This method can be used for the determination of molar masses of Biomolecules (which are generally not stable at higher temperatures) and for polymers (which have poor solubility).
Examples for osmosis:
a) Raw mango placed in concentrated salt solution loses water and shrink.
b) Wilted flowers revive when placed in fresh water
c) Blood cells collapse when suspended in saline water.
d) The preservation of meat by salting and fruits by adding sugar protect against bacterial action. Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrinks and dies.

## Isotonic, hypertonic and hypotonic solutions

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by a semi-permeable membrane, no osmosis occurs.

For e.g. our blood cells are isotonic with $0.9 \%$ (mass/volume) sodium chloride solution, called normal saline solution. So it is safe to inject intravenously.

A solution having higher osmotic pressure than another is called hypertonic solution. While a solution having lower osmotic pressure than another is called hypotonic solution.

If we place our blood cells in a solution containing more than $0.9 \%$ (mass/volume) sodium chloride solution, water will flow out of the cells and they would shrink. On the other hand, if they are placed in a solution containing less than $0.9 \%$ (mass/volume) NaCl , water will flow into the cells and they would swell.

## Reverse osmosis and water purification

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. Now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called reverse osmosis and is used in desalination of sea water.

When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. Commonly used SPM is cellulose acetate. A schematic representation of reverse osmosis is as follows:


## ABNORMAL MOLARMASS

The molar mass obtained by colligative property measurement is incorrect, if there is association or dissociation of particles. Such molar masses are called abnormal molar masses.

For e.g. acetic acid dimerises in benzene due to hydrogen bonding. So the number of molecules in solution decreases and hence the colligative property decreases and molecular mass increases.

In order to correct the abnormal molar masses, van't Hoff introduced a factor called van't Hoff factor (i). It is defined as:
$\mathrm{i}=\frac{\text { Normal Molar mass }}{\text { Abnormal molar mass }}$
Or, $\quad i=\underline{\text { Observed colligative property }}$
Calculated colligative property
Or, $\quad \mathrm{i}=$ Total number of moles of particles after association/dissociation
Number of moles of particles before association/dissociation In the case of association, the value of $\mathrm{i}<1$ and in dissociation, the value of $\mathrm{i}>1$. Thus for $\mathrm{NaCl}, \mathrm{i}=2$, for $\mathrm{K}_{2} \mathrm{SO}_{4}, \mathrm{i}=3$, for $\mathrm{CaCl}_{2}, \mathrm{i}=3$ and for acetic acid in benzene, $\mathrm{i}=1 / 2$ Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:

1. Relative lowering of vapour pressure, $\frac{\Delta P}{P_{1}{ }^{0}}=\frac{i \times W_{2} \times M_{1}}{W_{1} \times M_{2}}$
2. Elevation of Boiling point $\left(\Delta T_{b}\right)=i . K_{b} . m$
3. Depression of freezing point $\left(\Delta T_{f}\right)=\mathrm{i} . \mathrm{K}_{\mathrm{f}} \cdot \mathrm{m}$
4. Osmotic Pressure $(\pi)=i . C R T$
