

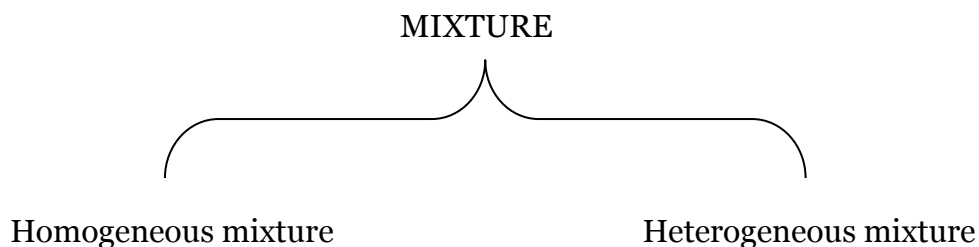
Solution and Colligative properties

Solution = Solvent + Solute

Solvent- A solvent is a substance which has the same state of aggregation as that of the solution.

Solute – A solute is a substance which is dissolved in the solvent.

Solution – A solution is a homogeneous mixture of two or more components (solutes). E.g. In a **solution** in which carbon dioxide is dissolved in water, the water is the solvent and the carbon dioxide is the solute.



Homogeneous mixture: A homogeneous mixture consist of a single phase which has property that may differ drastically from those of the individual components.

Heterogeneous mixture: A heterogeneous mixture consist of distinct phases and the observed properties are just the sum of the properties of individual components.

When two or more chemically non reacting substances are mixed, they form mixture.

According to the no. of components present in the solution, the solution can be **binary**, **ternary** or **quaternary**. Thus a solution may be regarded as single phase containing more than one phase.

Types of solution:

Depending upon the physical state of solvent, solution can be categorized as_____

1. Gaseous solution: solvent is in gaseous state.

- i) Gas in Gas- Mixture of oxygen and nitrogen gases
- ii) Liquid in Gas - Chloroform mixed with nitrogen gas
- iii) Solid in Gas - Camphor in nitrogen gas

2. Liquid solution: solvent is in liquid state.

- i) Gas in Liquid - Oxygen dissolved in water
- ii) Liquid in Liquid- Ethanol dissolved in water
- iii) Solid in Liquid - Glucose dissolved in water

3. Solid solution: solvent is in solid state

- i) Gas in Solid - Solution of hydrogen in palladium
- ii) Liquid in Solid - Amalgam of mercury with sodium
- iii) Solid in Solid - Copper dissolved in gold



SOLUBILITY

Solubility is the maximum amount of solute that can be dissolved in a given amount of solvent at a given temperature.

- Solubility depends on several factors:

1. Polarity of the solute and solvent

Remember: “like dissolves like”

- i. polar solutes dissolve in polar solvents
- ii. Non-polar solutes dissolve in non-polar solvents
- iii. Stronger inter molecular forces between the solute and solvent allow more solute to dissolve

2. Temperature

- i. Solubility of many (but not all) solids in liquids increases in high temperatures.
- ii. Solubility of gases in liquids decreases in high temperatures

3. Pressure (for gases)

i. solubility increases under high pressure

There is a limit to how much solute will dissolve in a solvent:

1. When a solution contains less than the maximum amount of solute that will dissolve, we say the solution is **unsaturated**
2. When a solution contains the maximum amount of solute that will dissolve, we say the solution is **saturated**.
3. When a solution contains more than the maximum amount of solute it should be able to dissolve (done by dissolving at high temp, then cooling), we say the solution is **supersaturated**.

The Effect of Temperature on Solubility

- Many, but not all, solid solutes are more soluble in liquids at higher temperatures

Ex. Chocolate milk mix dissolves better in hot milk than in cold milk.

- In general, gases are less soluble in liquids at higher temperatures.

Ex. A glass of hot water has more air bubbles than a glass of cold water

Effect of Pressure on Solubility of Gases

Generally, the solubility of a gas increases with increased external pressure.

Solubility is directly proportional to pressure...so if we double the pressure, solubility will be doubled.

This relationship is known as Henry's Law:

$$S = kP$$

Henry's law –Statement – solubility of gas in a liquid at constant temperature is proportional to the pressure of the gas above the solution.

Mathematical expression

$$S \propto P$$

$$\text{So } S = kP$$

Where S is solubility of the gas in mol/dm³

P is pressure of the gas in atmosphere.

K is constant of proportionality. i.e. Henry's constant. If P = 1 atm. Then S = k

If we use the mole fraction of a gas in the solution as a measure of its solubility, then it can be said that the **mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.** The most commonly used form of Henry's law. It is expressed as:

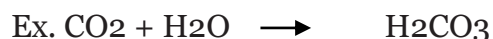
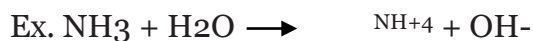
$$p = K_H x$$

Here K_H is the Henry's law constant.

Henry's Law works for most gases, EXCEPT gases that react with water

- Gases that react with water will have higher solubilities than predicted by Henry's

Law-



➤ Methods of expressing the concentration of solution-

1) Percentage by mass or weight (W/W) – The mass of solute in gram dissolved in solvent to form 100 gram of solution is called as Mass percentage.

Formula:

$$\% \text{ by mass of solute} = \frac{\text{mass of solute} \times 100}{\text{mass of solution}}$$

Where

Mass of solution = Mass of solute + Mass of solvent

It is independent of temperature as it does not contain term volume

2) Percentage by volume (v/v): It is defined as the ratio of number of parts by volume of the solute to one hundred parts by volume of the solution.

Formula:

$$\% \text{by volume of solute} = \frac{\text{vol. of solute} \times 100}{\text{Vol. of solution}}$$

3) Mole fraction (x): The mole fraction of any component of solution is defined as the ratio of number of moles of that component present in the solution to the total number of moles of all the components of the solution.

Mathematical expression of x:

For binary solution-

n_1 = number of moles of species 1

n_2 = number of moles of species 2

$$X_1 = \frac{n_1}{n_1 + n_2} = \text{mole fraction of species 1}$$

$$X_2 = \frac{n_2}{n_1 + n_2} = \text{mole fraction of species 2}$$

$$X_1 + X_2 = 1$$

Note:

1. Sum of mole fraction of all components of any solution is always unity.

2. Mole fraction is temperature independent.

4). Molarity (M) – it is defined as the no. of moles of solute present in the 1 liter of solution.

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in liters}}$$

Note:

1. Molarity is expressed in moles per liter
2. It depends on temperature as it contains the term volume.

5). Molality (m) – it is defined as the no. of moles of solute present in 1 kg of solvent.

$$\text{Molality(m)} = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

Note: Best method to express concentration as it is temperature independent.

6). Normality (N) – it is defined as the no. of equivalents of solute present in 1 liter of solution.

$$N = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution in litres}}$$

$$\text{equivalents} = \frac{\text{grams of solute}}{\text{equivalent mass of solute}}$$

Relation between molarity and Normality.

$$N = n \times M$$

Where n = acidity / basicity

(Note: normality is temperature dependent)

7). Parts per million (ppm):

This is a way of expressing very dilute concentrations of substances. Just as per cent means out of a hundred, so parts per million or ppm means out of a million.

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

➤ Vapour pressure:

It can be defined as the pressure exerted by the vapour of the liquid when liquid – vapour equilibrium is established.

At equilibrium—

Rate of vapourisation = rate of condensation

And the pressure of the vapour at this stage is called vapour pressure. It is the max. pressure produced by the liquid.

Vapour pressure is the characteristics property of any liquid and it is constant at constant temperature.

Vapour pressure \propto temperature

It does not depend upon quantity and type of vessel (**Intensive property**).

The liquid having high attracting forces in their molecules will have lesser vapour pressure, i.e. less volatile.

Vapour pressure of solution

Consider a binary solution of two volatile liquids A & B. when taken in a closed vessel, both the components would evaporate & eventually an equilibrium would be established between vapour phase and liquid phase. Let the total vapour pressure at this stage be P_{total} and P_a and P_b be the partial vapour pressures of the two components A and B respectively.

	A	B
Pressure in pure state-	$P^{\circ}a$	$P^{\circ}b$
Mole fraction in sol.- X_a	X_b	
Partial pressure -	p_a	p_b

Raoult's law: it is a law of thermodynamics. According to this law the partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.

$$p_a = X_a P^{\circ}a$$

$$p_b = X_b P^{\circ}b$$

$$P_{\text{total}} = p_a + p_b$$

$$= X_a P^{\circ}a + X_b P^{\circ}b$$

We know, $X_a + X_b = 1$

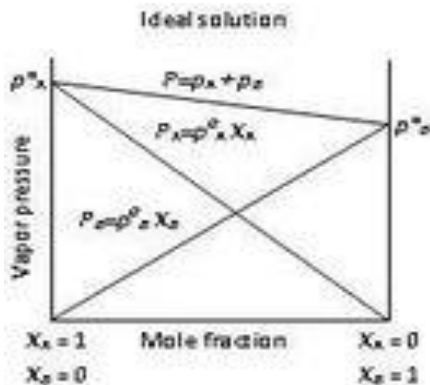
$$\Rightarrow P_{\text{total}} = X_a P^{\circ}a + (1 - X_a) P^{\circ}b$$

\Rightarrow Total pressure of any solution can be changed by changing mole fraction of its constituents.

The pressure of any solution lies between pressures of pure A to pressure of pure B

Graphical representation of Raoult's law :

Assuming A is more volatile than B



For $X_a = 1$; V.P = $P^{\circ}a$

For $X_b = 1$; V.P = $P^{\circ}b$

Non-volatile substances has V.P = 0

Dalton's law: The composition of vapour phase in equilibrium with the solution is determined applying Dalton's law of partial pressure. Dalton's law shows the

relationship between partial pressures of constituents in liquid phase to the mole fraction of constituents in vapour phase.

Let Y_a & Y_b the mole fraction of vapour A & vapour B respectively. Then,

$$Y_a = p_a / P_{\text{total}}$$

$$Y_b = p_b / P_{\text{total}}$$

$$\text{Where } P_{\text{total}} = X_a P^{\circ}_a + X_b P^{\circ}_b$$

This shows the relation between Raoult's law & Dalton's law.

Note: Raoult's law is applicable only for ideal solutions. Real solutions (non-ideal solutions) do not obey Raoult's law.

➤ Ideal and Non-ideal Solution-

SOLUTION

Ideal solution

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

$$\Delta H_{\text{mix}} = 0$$

Real solution

$$\Delta V_{\text{mix}} \neq 0$$

$$\Delta H_{\text{mix}} \neq 0$$

Ideal solutions: the solution which follow Raoult's law at all temperature and all mole fractions is regarded as ideal solution.

Conditions...

i) $\Delta H_{\text{mix}} = 0$

iii) Vol. of solute + Vol. of solvent = Vol. of solution

ii) $\Delta V_{\text{mix}} = 0$

iv) There should not be association / dissociation of molecule

Note: Very dilute solution is regarded as ideal solution

Real solution: The real solution is the solution which do not follow Raoult's law.

$$\Delta V_{\text{mix}} \neq 0$$

$$\Delta H_{\text{mix}} \neq 0$$

Molecules usually associate or dissociate in the solution. It is also called as non-ideal solutions. Real solutions show positive or negative deviation from Raoult's law.

Real/Non ideal solution

Positive deviation

Negative deviation

$$P_{\text{total}} > X_a P^{\circ}_a + X_b P^{\circ}_b$$

$$P_{\text{total}} < X_a P^{\circ}_a + X_b P^{\circ}_b$$

$$\Delta V_{\text{mix}} > 0$$

$$\Delta V_{\text{mix}} < 0$$

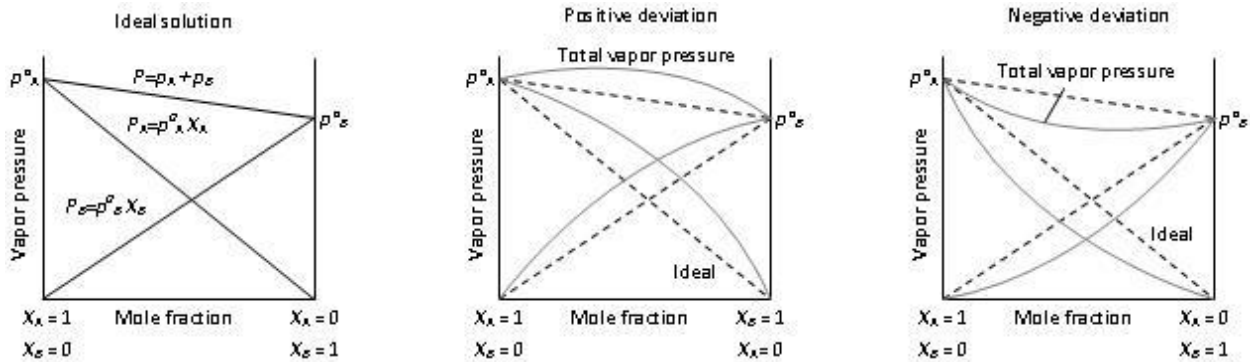
$$\Delta H_{\text{mix}} > 0$$

$$\Delta H_{\text{mix}} < 0$$

Sol. Shows Cooling effect

Sol. Shows Heating effect

Raoult's law for ideal sol. & non ideal sol (both for +ive & -ive deviation) is shown graphically as



Azeotropes: When a real solution is boiled at some point, the solution will boil without any change in its composition and without any change in its boiling point. At this point, the solution is called an azeotropic mixture or constant boiling mixture.

For positive deviation - at any certain pt. vapour pressure of the solution will be maximum and normal boiling pt. will be minimum.

E.g. EtOH(95%) + H₂O(5%)

For negative deviation - we get maximum normal boiling point azeotropes.

E.g., HNO₃ (68%)+H₂O (32%)

In azeotropes composition of liquid phase and vapour phase is identical. so if azeotropic mix is vaporized we get the vapours of same composition. And when the vapours are condensed, we get the liquid of same composition. So the mixture boils as if were a pure liquid.

Min. b.pt azeotrope-b.pt is lower than each of the pure components.

Max.b.pt azeotrope-b.pt is higher than each of the pure components.

➤ Colligative properties:

We know that vapour pressure of solution decreases when a non- volatile solute is added to a volatile solvent. These are many properties of the solutions which are connected with the decrease of vapour pressure. These properties are called colligative properties. Colligative properties depend only on the number of solute particles in solution and not on the nature of the solute particles.

Four Colligative Properties

1. Relative lowering of vapour pressure of solvent in solution
2. Elevation of boiling point of solvent in solution
3. Depression of freezing point of solvent in solution
4. Osmotic pressure

Relative lowering of vapour pressure:

When a nonvolatile solute is added to the solution the vapour pressure is lowered due to following reason

% surface area occupied by the solvent decreases, thus the rate of evaporation decreases and hence vapour pressure decreases.

Solute (non-volatile)

$$P^{\circ}a = 0$$

$$Xa$$

Solvent

$$P^{\circ}b$$

$$Xb$$

$$P_{total} = Xa P^{\circ}a + Xb P^{\circ}b$$

$$= Xa \cdot 0 + Xb P^{\circ}b$$

$$= Xb P^{\circ}b \quad \dots\dots\dots(1)$$

Since $X_b < 1$

So $P_{\text{total}} < P^{\circ}_b$

Hence, on adding solute mole fraction of solvent decreases, so vapour pressure of the solution will also decrease.

Lowering of vapour pressure = $P^{\circ}_b - P_{\text{total}}$

Higher the moles of solute greater will be lowering.

Relative lowering of vapour pressure = $\frac{P^{\circ}_b - P_{\text{total}}}{P^{\circ}_b}$

From eqn (1) $P_{\text{total}} = X_b P^{\circ}_b = (1 - X_a) P^{\circ}_b$

Hence, $P_{\text{total}} = P^{\circ}_b - X_a P^{\circ}_b$

$\Rightarrow P^{\circ}_b - P_{\text{total}} = X_a P^{\circ}_b$

so $\frac{P^{\circ}_b - P_{\text{total}}}{P^{\circ}_b} = X_a = \frac{N_a}{N_a + N_b}$

\Rightarrow Relative lowering of vapour pressure = mole fraction of solute added

- Mole fraction is independent of temperature so Relative lowering of vapour pressure is also independent of temperature.

lowering of vapour pressure \propto mole fraction of solute

Elevation of boiling point (ebullioscopy)

The temperature at which vapour pressure of a solvent is equal to atmospheric pressure is called boiling point of that liquid on adding non-volatile solute V.P. of solvent will decrease, hence boiling point of the solvent will increase.

Definition - Elevation of boiling point is the difference between boiling points of solution and that of pure solvent.

$$\Delta T_b = K_b m \dots \dots \dots (2)$$

ΔT_b – elevation of boiling point

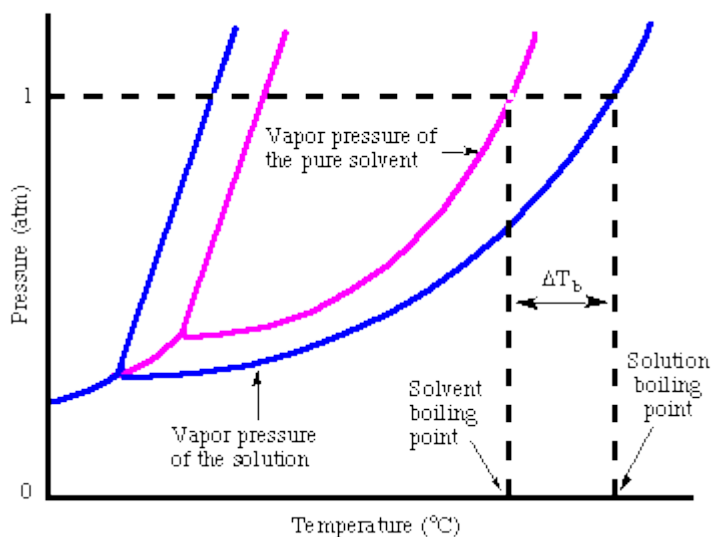
m – molality
 K_b – molal boiling point elevation constant or
 Ebullioscopic constant

The elevation of B.P. of a solvent of non-electrolyte is proportional to its molality and equimolal sol. of all the substances in the same solvent will show equal elevation of boiling point.

$$K_b = \frac{RT_b^2}{1000Lv}$$

where R is the gas constant, and T_b is the boiling temperature of the pure solvent [in K], L is latent heat of vapourisation in cal/gm.

Phase Diagram for a Solution and the Pure Solvent Indicating the boiling point elevation -



Depression of freezing point

Freezing point of any substance is defined as the temperature at which the vapour of its liquid is equal to the vapour pressure of the corresponding solid. since the addition of non-volatile solute always lower the V.P. of a solvent therefore it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature.

$$\Delta T_f = \text{F.P. of solvent} - \text{F.P. of solution}$$

$$\Delta T_f = K_f m \dots \dots \dots (3)$$

ΔT_f – depression in freezing point

m – molality

K_f – molal freezing point depression constant or cryoscopic constant

$$K_f = \frac{RT_f^2}{1000L_f}$$

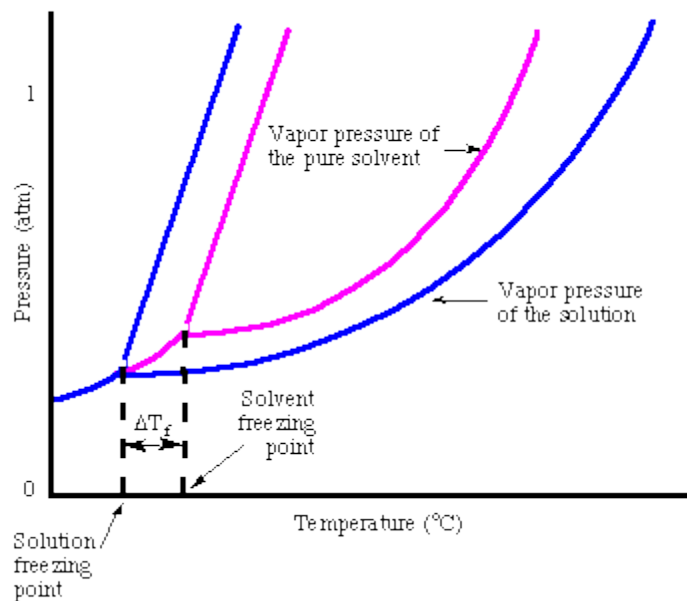
where R is the gas constant, and T_f is the freezing temperature of the pure solvent [in K], L_f is latent heat of vapourisation in cal/gm.

Note: normally $K_f > K_b$

$$K_f(\text{H}_2\text{O}) = 1.86$$

$$K_b(\text{H}_2\text{O}) = 0.515$$

Phase Diagram for a Solution and the Pure Solvent Indicating the Freezing Point Depression -



➤ Osmotic pressure:

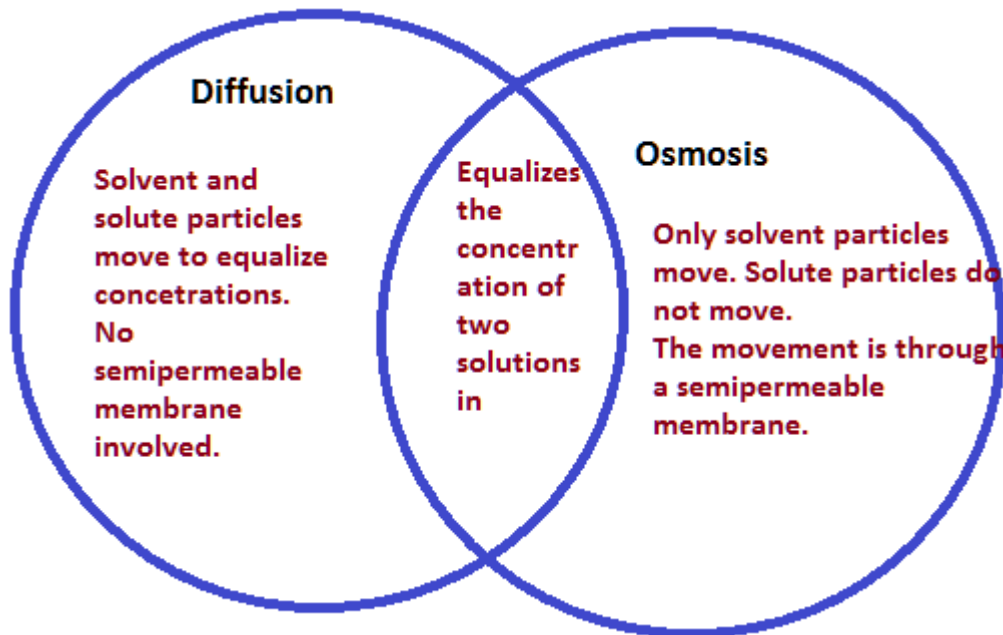
Semi permeable membrane – it is a membrane which is selective in nature. It allows to pass through them only solvent particles.

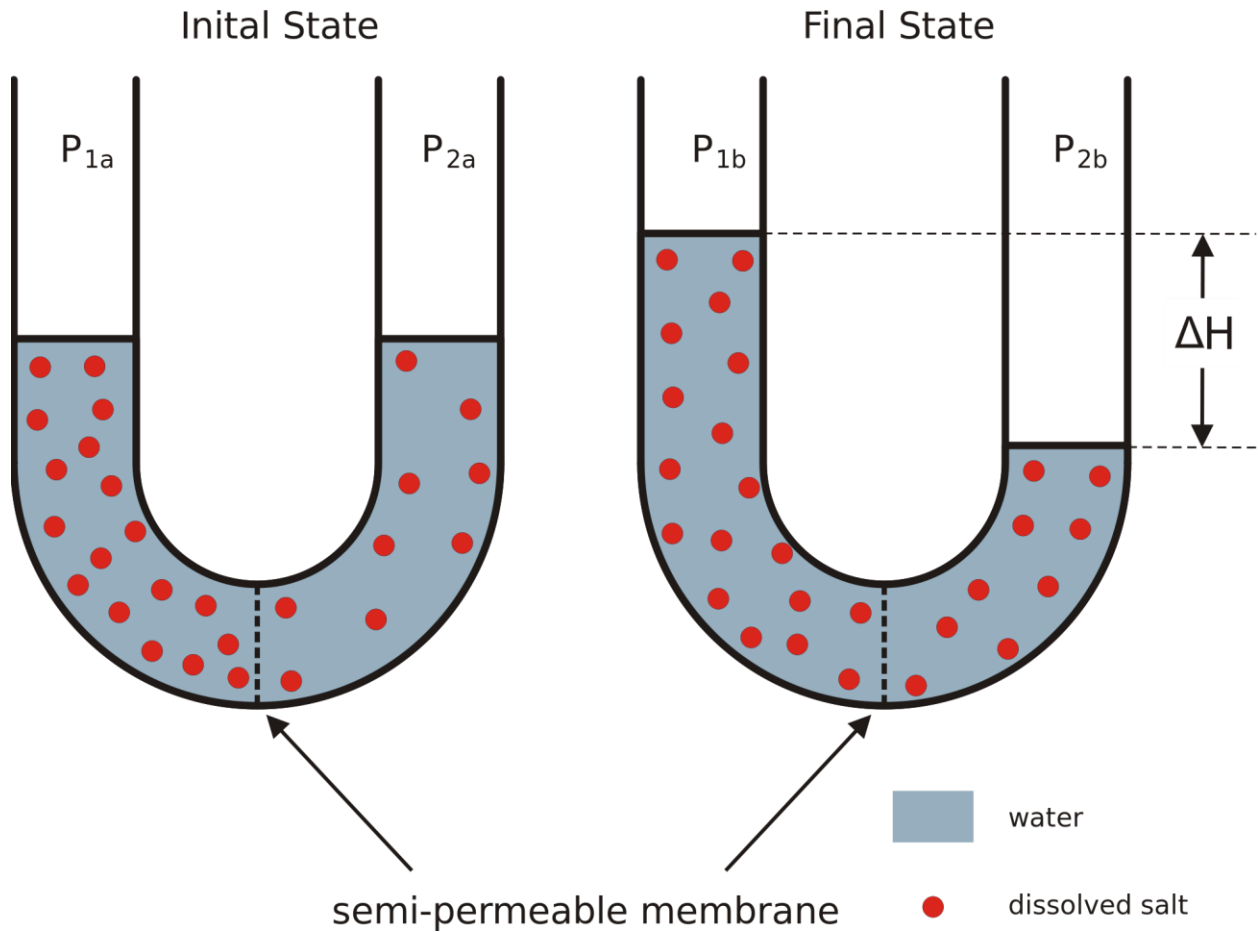
Osmosis: it is defined as the spontaneous flow of solvent molecules through semi permeable membrane from a dilute to concentrated solution.

Osmosis occurs from –

- Low conc. To high conc.
- High V.P. to low V.P.

Osmosis Vs Diffusion –





Osmotic pressure: The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution.

OR

It can be defined as the hydrostatic pressure built on the solution which just stop the osmosis.

Osmotic pressure = Hydrostatic pressure (at equilibrium)

$$\Pi = dg\Delta H$$

Where, d- density of solution

g - gravity

ΔH - difference of height levels

Reverse osmosis: if we apply external pressure more than osmotic pressure on high concentration side then solvent particles start flowing from high concentration to low concentration side. This is called reverse osmosis.

Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity. For dilute solutions, it has been found experimentally that **osmotic pressure is proportional to the molarity, C of the solution at a given temperature T .**

$$\Pi \propto C \quad (C - \text{concentration})$$

$$\Rightarrow \Pi = CRT = (n/V)RT$$

Π – Osmotic pressure

R – Gas constant

T – Temperature

n – No. of moles

V – Volume of solution

• Higher the concentration greater will be osmotic pressure.

• Osmosis occurs from low osmotic pressure to high osmotic pressure

Isotonic solution: if two solutions have identical osmotic pressure then it will be called as isotonic solution.

Hypertonic solution: if a solution has high osmotic pressure i.e. low V . pressure w.r.t another solution then it will be hypertonic solution.

Hypotonic solution: if a solution has low osmotic pressure i.e. high V . pressure w.r.t another solution then it will be hypotonic solution.

Osmosis occurs hypotonic to hypertonic solution

1. If the medium is *hypotonic* relative to the cell cytoplasm — the cell will gain water through osmosis.
2. If the medium is *isotonic* — there will be no net movement of water across the cell membrane.
3. If the medium is *hypertonic* relative to the cell cytoplasm — the cell will lose water by osmosis.

➤ Abnormal molar masses and abnormal colligative properties:

We have learnt all the colligative properties w.r.t ideal solution. In ideal solution there is no association or dissociation of molecule.

ABNORMAL COLLIGATIVE PROPERTIES

The colligative properties of solutions depend on the number of solute particles present in solution. Various relations derived for colligative properties hold good in dilute solutions only when there is no change in molecular state of solute. In case the total number of particles of the solute changes in solution, the colligative property shall also change accordingly. The number of particles in solution may change in two ways:

(i) **By dissociation:**

(ii) **By association:**

When there is association or dissociation of solute molecules in the solution then the solution is regarded as non-ideal solution. The study of such solutions is done under the concept of abnormal colligative properties.

What is abnormal molar mass....?

Due to association or dissociation of molecules the molar mass of a substance calculated from its colligative properties is either lower or higher than the expected or normal value. Such molar mass is called abnormal molar mass.

In 1880 van't Hoff introduced a factor i , known as the van't Hoff factor, to account for the extent of dissociation or association. This factor i is defined as:

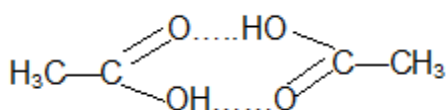
$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$
$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

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

Here abnormal molar mass is the experimentally determined molar mass and calculated colligative properties are obtained by assuming that the non-volatile solute is neither associated nor dissociated.

Solute

ASSOCIATION $i < 1$



E.g. urea, glucose, sucrose

Colligative properties with van'thoff factor-

$$1. \text{ Relative lowering of vapour pressure} = \frac{P^{\circ}_b - P_{\text{total}}}{P^{\circ}_b} = \frac{iX_a}{\frac{N_a + N_b}{N_a + N_b}} = \frac{iN_a}{N_a + N_b}$$

$$2. \text{ Elevation of boiling point} = \Delta T_b = iK_b m$$

$$3. \text{ Depression of freezing point} = \Delta T_f = K_{bf} m$$

$$4. \text{ Osmotic pressure} = \Pi = iCRT = i(n/V)RT$$

DISSOCIATION $i > 1$

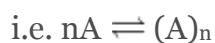


E.g. ionic solutes

Degree of Association:

The fraction of the total number of molecules which combine to form bigger molecule.

Consider one mole of solute dissolved in a given volume of solvent. Suppose n simple molecules combine to form an associated molecule,



Let a be the degree of association, then,

The number of unassociated moles = 1-a

The number of associated moles = a/n

Total number of effective moles = $1-a+a/n$

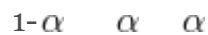
$$i = \frac{1 - \alpha + \alpha/n}{1}$$

$$i = 1 - a(1 - 1/n)$$

Hence $i < 1$

Degree of Dissociation

Degree of dissociation means *the fraction of the total number of molecules which dissociates in the solution, that is, breaks into simpler molecules or ions.*



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

Hence, $i = (1 + \alpha)/1$

$$i = 1 + \alpha = 1 + (2 - 1)\alpha$$

In general, $i = 1 + (n - 1)\alpha$, Where, n = number of particles (ions) formed after dissociation

Hence $i > 1$.