

1. 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 | Examples |
|-------------------|--------|---------|---|
| Gaseous solutions | Gas | Gas | Mixture of O ₂ and 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 the following ways:

- (i) **Mass percentage (w/w):** It is defined as the mass of the component present in 100g of the solution.

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

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 (v/v):** It is defined as the volume of a component present in 100 mL of the solution.

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

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 (w/v):** It is the mass of solute dissolved in 100 mL of the solution. It is commonly used in medicine and pharmacy.

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

- (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.

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

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 $\mu\text{g mL}^{-1}$ or ppm. [μg is microgram]

(v) **Mole fraction (χ):** It is defined as the ratio of the number of moles of a particular component to the total number of moles of the solution.

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

For example, in a binary solution, if the number of moles of A and B are n_A and n_B respectively,

$$\text{then, the mole fraction of A } (\chi_A) = \frac{n_A}{n_A + n_B}$$

$$\text{and that of the component B } (\chi_B) = \frac{n_B}{n_A + n_B}$$

$$\chi_A + \chi_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

i.e. in a given solution sum of the mole fractions of all the components is unity. If there are i components, then,

$$\chi_1 + \chi_2 + \chi_3 + \dots + \chi_i = 1$$

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.

$$\text{i.e. Molarity (M)} = \frac{\text{Number of moles of solute (n)}}{\text{Volume of solution in litre (V)}}$$

For example, 1 M (molar) NaOH solution means that 1 mol of NaOH (40g) 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.

$$\text{i.e. Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

For example, 1 molal (m) solution of KCl means that 1 mol (74.5 g) of KCl is dissolved in 1 kg of water.

Among the different methods for expressing the concentration of solution, **mass percentage, ppm (in terms of mass), mole fraction and molality are temperature independent**; while **molarity, mass by volume percentage and volume percentage** are temperature dependent. This is because *volume of solution 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 at a particular temperature. It depends upon the nature of solute, nature of the 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

When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution. Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallisation. After sometime, the rate

of dissolution and crystallization becomes equal and a dynamic equilibrium is reached. At this stage the concentration of solute in the solution remain constant and such a solution is called saturated solution.

A solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution. For such a solution, the concentration of the solution is equal to its solubility.

A solution in which more solute can be dissolved at the same temperature is called an unsaturated solution.

Effect of temperature on the solubility of a solid in a liquid

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 Chatelier's Principle. In general, *in a nearly saturated solution, if the dissolution process is **endothermic** ($\Delta_{sol} H > 0$), the solubility should **increase** with rise in temperature and if it is **exothermic** ($\Delta_{sol} H < 0$) the solubility should **decrease** with temperature.*

Effect of pressure on the solubility of a solid in a liquid

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.

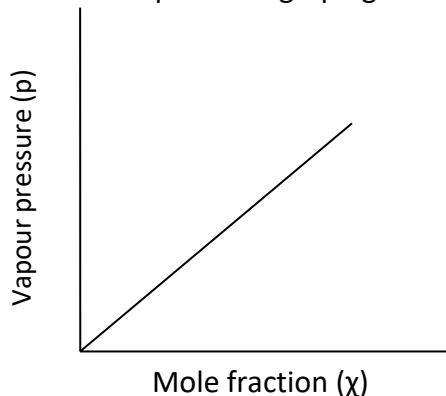
A quantitative relation between pressure and solubility of a gas in a liquid was first given by Henry, which is known as **Henry's law**. "*The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas*".

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

$$p = K_H \chi$$

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 K_H increases, the solubility of the gas in the liquid decreases.

A graph of partial pressure (p) of the gas against mole fraction (χ) of the gas in solution is a straight line as follows. The slope of the graph gives the value of K_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 water rather than in warm water.

Applications of Henry's law

1. To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
2. A medical condition known as *bends* in *scuba divers*. To avoid bends, the cylinders used by scuba divers are filled with air diluted with helium (The composition of the air in the cylinders used by scuba divers is 32.1% oxygen, 56.2% nitrogen and 11.7% helium).
3. A medical condition known as *anoxia* in people living at high altitudes and in mountaineers or climbers.

Effect of Temperature on the solubility of a gas in a liquid

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase. So the process of dissolution can be considered similar to condensation, which is exothermic. Hence solubility decreases with increase of temperature.

Vapour Pressure of a liquid

In a liquid, the molecules with higher energy are escaped to vapour phase. This process is called **evaporation**. As the density of the vapour increases, the molecules collide with each other and so their energy decreases and returns to the liquid state. This process is called **condensation**.

After some time, the rate of evaporation becomes equal to rate of condensation and the two processes attain equilibrium. At this condition, the pressure exerted by the vapour is called **vapour pressure**. So vapour pressure is defined as *the pressure exerted by the vapour in equilibrium with its own liquid*. It depends on the nature of the liquid and the temperature. As the temperature *increases*, the vapour pressure also *increases*.

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 Francois Martre Raoult (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_{total} be the total vapour pressure. Let χ_1 and χ_2 be the mole fractions of the two components 1 and 2 respectively.

Then according to Raoult's law,

for component 1, $p_1 \propto \chi_1$

or, $p_1 = p_1^0 \cdot \chi_1$

and for component 2, $p_2 \propto \chi_2$

or, $p_2 = p_2^0 \cdot \chi_2$

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 (p_{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

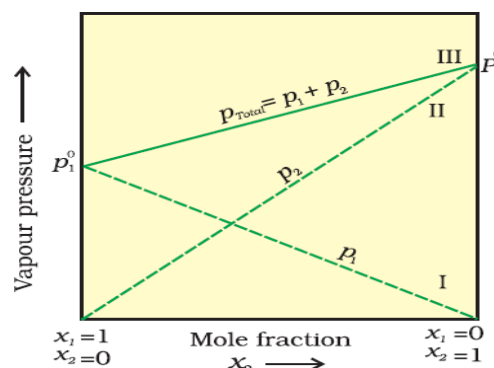
$$p_{\text{total}} = \chi_1 \cdot p_1^0 + \chi_2 \cdot p_2^0$$

$$= (1 - \chi_2) p_1^0 + \chi_2 \cdot p_2^0$$

$$\text{Or, } p_{\text{total}} = p_1^0 + (p_2^0 - p_1^0) \chi_2$$

Plots of p_1 or p_2 against the mole fractions χ_1 and χ_2 give straight lines (I and II). Similarly the plot of p_{total} versus χ_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:



$$p_1 = y_1 p_{\text{total}} \text{ and } p_2 = y_2 p_{\text{total}}$$

$$\text{In general, } p_i = y_i p_{\text{total}}$$

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 $P_1 = \chi_1 \cdot p_1^0$. According to Henry's law, solubility of a gas in a liquid is given by $p = K_H \chi$.

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 p_1^0 .

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 vapour pressure of a component in the solution is equal to the vapour pressure of the pure component multiplied by its mole fraction in the solution.

$$\text{i.e. } p_1 = p_1^0 \cdot \chi_1 \text{ and } p_2 = p_2^0 \cdot \chi_2$$

For such solutions, no heat change occurs during the mixing of the pure components [i.e. $\Delta_{\text{mix}}H = 0$].

Also, the volume of the solution is equal to the sum of the volumes of the components. Or, there is no change

in the volume of the solution during mixing of the components [i.e. $\Delta_{\text{mix}}V = 0$]
Thus **for an ideal solution, $p_1 = p_1^0 \cdot \chi_1$, $p_2 = p_2^0 \cdot \chi_2$, $\Delta_{\text{mix}}H = 0$ and $\Delta_{\text{mix}}V = 0$**

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 shows *positive deviation* from Raoult's law and if it is lower, it shows *negative deviation* from Raoult's law.

(i) *Solutions which show positive deviation from Raoult's law:*
For such solutions, **$p_1 > p_1^0 \cdot \chi_1$, $p_2 > p_2^0 \cdot \chi_2$, $\Delta_{\text{mix}}H > 0$ and $\Delta_{\text{mix}}V > 0$**

Here 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.

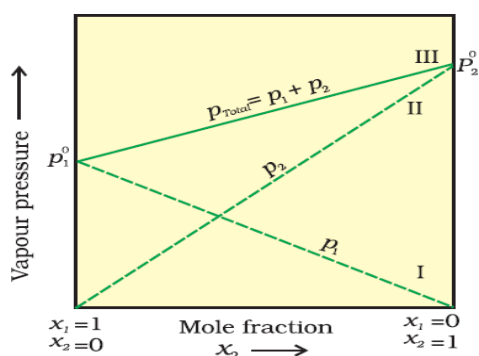
E.g. solutions of ethanol and acetone, acetone and CS_2 , acetone and CCl_4 etc.

(ii) *Solutions which show negative deviation from Raoult's law:*
For such solutions, **$p_1 < p_1^0 \cdot \chi_1$, $p_2 < p_2^0 \cdot \chi_2$, $\Delta_{\text{mix}}H < 0$ and $\Delta_{\text{mix}}V < 0$**

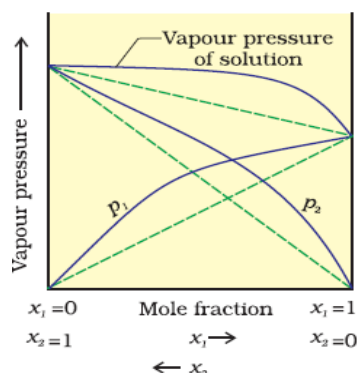
Here A-B interactions are stronger than A-A and B-B interactions. i.e. solute-solvent interactions are stronger than solute-solute interaction and solvent-solvent interaction. So number of molecules escaped to vapour phase decreases and hence the vapour pressure of the solution decreases.

E.g. solution of phenol and aniline, chloroform and acetone etc.

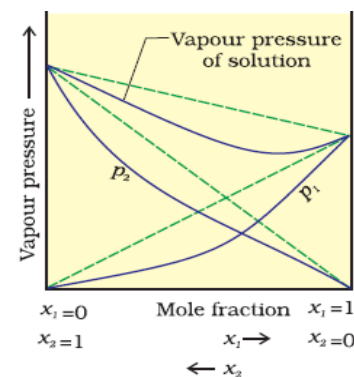
The plots of vapour pressure curves for ideal solution, solutions which show positive deviation and negative deviation from Raoult's law are as follows:



Ideal Solutions



Solutions showing Positive deviation from Raoult's law



Solutions showing Negative deviation from Raoult's law

Azeotropes [Constant Boiling Mixtures]

These 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% aqueous ethanol solution by volume at 78.2°C [351.35 K].

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.



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 solvent 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 in solution.**

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, χ_1 be its mole fraction, p_1^0 be its vapour pressure in the pure state. Then according to

Raoult's law, $p_1 \propto \chi_1$

or, $p_1 = p_1^0 \chi_1$

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

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COLLIGATIVE PROPERTIES AND DETERMINATION OF MOLAR MASS

The properties which depend only on the relative 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 (Δp).

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 [V.P of solution = V.P of the solvent in the solution, since the solute is non-volatile].

Then according to Raoult's law, $p_1 = p_1^0 \cdot \chi_1$

The lowering of vapour pressure of the solvent (Δp) = $p_1^0 - p_1$

$$= p_1^0 - p_1^0 \chi_1$$

$$\text{Or, } \Delta p = p_1^0 (1 - \chi_1)$$

But $\chi_1 + \chi_2 = 1$. Therefore $1 - \chi_1 = \chi_2$

$$\text{So } \Delta p = p_1^0 \cdot \chi_2$$

$$\text{Or, } \frac{\Delta p}{p_1^0} = \chi_2, \text{ the mole fraction of the solute.}$$

$$\Delta p$$

Where $\frac{\Delta p}{p_1^0}$ 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.

$$\text{But } \chi_2 = \frac{n_2}{n_1 + n_2}$$

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.

$$\text{So, } \chi_2 = \frac{n_2}{n_1}$$

$$\text{Therefore, } \frac{\Delta p}{p_1^0} = \frac{n_2}{n_1}$$

$$\text{Or, } \frac{\Delta p}{p_1^0} = \frac{w_2 / M_2}{w_1 / M_1}$$

$$\text{Or, } \frac{\Delta p}{p_1^0} = \frac{w_2}{w_1} \times \frac{M_1}{M_2}$$

Where w_1 and w_2 are the masses and M_1 and M_2 are the molar masses of solvent and solute respectively.

2. Elevation of Boiling Point (ΔT_b)

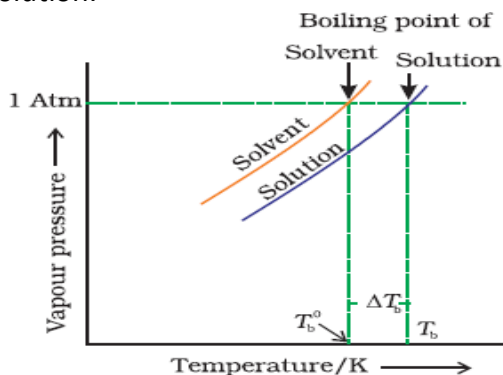
When a liquid is heated, its vapour pressure increases. At a particular temperature, the vapour pressure becomes equal to the external pressure (atmospheric pressure). This temperature is called boiling point of the liquid. So boiling point is the temperature at which its vapour pressure becomes equal 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 (ΔT_b) and that of the pure solvent (T_b^0) is called elevation of boiling point (T_b).

i.e. ΔT_b = Boiling point of solution – Boiling point of pure solvent

$$\text{Or, } \Delta T_b = T_b - T_b^0$$

If we plot a graph between the vapour pressure and temperature, we get the following graphs for the pure solvent and the solution.



For dilute solutions, the elevation of boiling point is directly proportional to molality (m).

$$\text{i.e. } \Delta T_b \propto m$$

$$\text{or, } \Delta T_b = K_b \cdot m$$

Where K_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 (i.e. it is the increase in boiling point of a solution containing 1 mol of a solute in 1 kg of the solvent).

The unit of K_b is K kg/mol. For water, $K_b = 0.52 \text{ K kg/mol}$.

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

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

$$\text{Or, } \Delta T_b = \frac{1000 K_b \cdot w_2}{M_2 \cdot w_1}$$

Where w_1 = mass of solvent, w_2 = mass of solute, M_2 = molar mass of solute. By using this equation, we can calculate the molar mass of unknown solute.

3. Depression of Freezing point (ΔT_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. So the freezing point (f.p) of the solution is less than that of the pure solvent. The difference between the freezing point (f.p) of pure solvent (T_f^0) and that of the solution (T_f) is called depression of freezing point (ΔT_f).

$$\text{i.e. } \Delta T_f = T_f^0 - T_f$$

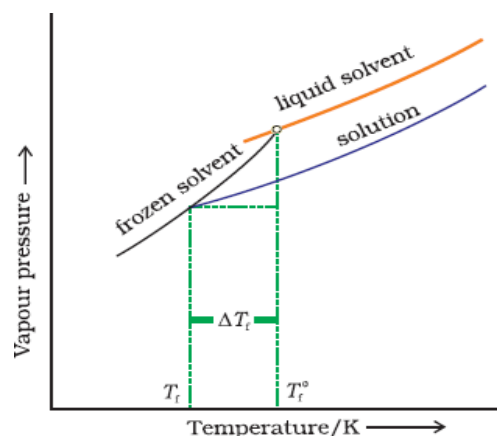
The vapour pressure – temperature graph representing the freezing point of pure solvent and solution is as follows:

For dilute solutions, it is found that the depression of freezing point (ΔT_f) is directly proportional to molality (m) of the solution.

$$\text{Thus } \Delta T_f \propto m$$

$$\text{Or, } \Delta T_f = K_f \cdot m$$

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



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freezing point for 1 molal solution. i.e. it is the depression in freezing point of a solution prepared by dissolving 1 mol of solute in 1 kg of solvent.

The unit of K_f is K kg/mol. For water, $K_f = 1.86$ K kg/mol.

We know that molality, $m = \frac{w_2 \times 1000}{M_2 \times w_1}$

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

Or, $\Delta T_f = \frac{1000 K_f \cdot w_2}{M_2 \cdot w_1}$

Where w_1 = mass of solvent, w_2 = mass of solute, M_2 = molar mass of solute. By using this equation, we can calculate the molar mass of an unknown solute.

4. Osmosis and Osmotic Pressure

Osmosis is the process of flow of solvent molecules from pure solvent to the 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 only solvent molecules is called a semi-permeable membrane. E.g. egg membrane, parchment, pig's bladder, all animal and plant membrane. Cellulose acetate is an example for artificial semi-permeable membrane.

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 π . 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. $\pi \propto CT$

Or, $\pi = CRT$

Here R is the universal gas constant ($R = 0.0821$ Latm/K/mol or $R = 0.083$ Lbar/K/mol).

But $C = n_2/V$, the concentration of the solution.

Therefore, $\pi = \frac{n_2 RT}{V}$

Or, $\pi V = n_2 RT$

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

Where V is the volume of the solution, w_2 is the mass of solute and 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:

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

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.

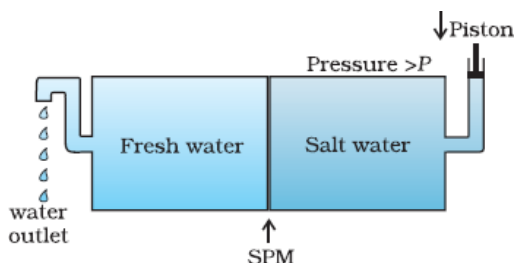
A solution having higher osmotic pressure than another is called hypertonic solution. While a solution having lower osmotic pressure than another is called hypotonic solution.

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. It 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 semi-permeable membrane is cellulose acetate. A schematic representation of reverse osmosis is as follows:



Reverse osmosis is also used in the purification of water.

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:

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

$$\text{Or, } i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

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

In the case of association, the value of $i < 1$ and in dissociation, the value of $i > 1$.

Thus for NaCl, $i = 2$, for K_2SO_4 , $i = 3$, for $CaCl_2$, $i = 3$ and for acetic acid in benzene, $i = \frac{1}{2}$

Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:

1. Relative lowering of vapour pressure, $\frac{\Delta p}{p_1^0} = i \cdot \frac{w_2}{w_1} \times \frac{M_1}{M_2}$
2. Elevation of Boiling point $(\Delta T_b) = i \cdot K_b \cdot m$
3. Depression of freezing point $(\Delta T_f) = i \cdot K_f \cdot m$
4. Osmotic Pressure $(\pi) = i \cdot CRT$

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