

## Concentration of Solution:

The Concentration of a Solution is defined as the relative amount of solute present in a solution.

It basically talks about how to find the amount of solute present in solvent which together forms solution. There are various methods used to find this,

### Methods of Expressing Concentration of Solutions

- Percentage by weight (w / w %)
- Percentage by volume (V / V%)
- Weight by volume (w /V%)
- Mole fraction (x)
- Parts per million (ppm)
- Molarity (M)
- Molality (m)
- Normality (N)
- Formality (F)

- **Percentage by Weight**

**Symbol:** (w / w %)

**Definition:** It is defined as the amount of solute present in 100 g of solution.

- **Percentage by Volume**

**Symbol:** (V / V %)

**Definition:** It is defined as the volume of solute present in 100 mL of solution.

- **Weight by Volume**

**Symbol:** (W / V %)

**Definition:** It is defined as the amount of solute present in 100 mL of solution.

Unit: mg/L

### Percent Concentration

a. Weight Percent  $\left(\frac{W}{W}\right) = \frac{\text{Weight Solute}}{\text{Weight Solution}} \times 100\%$

b. Volume Percent  $\left(\frac{V}{V}\right) = \frac{\text{Volume Solute}}{\text{Volume Solution}} \times 100\%$

c. Weight /Volume Percent  $\left(\frac{W}{V}\right) = \frac{\text{Weight Solute, g}}{\text{Volume Soln, L}} \times 100\%$

**Example:**

As an example consider 5 g sugar dissolved in 20 g of water. What is the w/w% concentration of sugar in this solution?

$$\frac{5 \text{ g sugar}}{25 \text{ g solution}} \times 100 = 20 \text{ w/w \%}$$

**• Mole Fraction**

**Symbol :** X ( lower-case Greek letter chi,  $\chi$ )

**Definition:** It is the ratio of the number of moles of solute and the total number of moles of solute and solvent.

Unit: No unit

**Formula:**

$$\text{Mole Fraction of Solute, } X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$\text{Mole Fraction of Solvent, } X_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$\text{Where, } X_{\text{solute}} + X_{\text{solvent}} = 1$$

**Mole Fraction (X):** This is the number of moles of a compound divided by the total number of moles of all chemical species in the solution.

$$X_{\text{solute}} = \frac{\text{Moles of Solute}}{\text{Total moles of all components}}$$

**Example:**

What are the mole fraction of the components of the solution formed when 92 g glycerol is mixed with 90 g water? (molecular weight of water = 18; molecular weight of glycerol = 92)

**Solution:**

$$90 \text{ g water} = 90 \text{ g} \times 1 \text{ mol} / 18 \text{ g} = 5 \text{ mol water}$$

$$92 \text{ g glycerol} = 92 \text{ g} \times 1 \text{ mol} / 92 \text{ g} = 1 \text{ mol glycerol}$$

$$\text{Total mol} = 5 + 1 = 6 \text{ mol}$$

$$X_{\text{water}} = 5 \text{ mol} / 6 \text{ mol} = 0.833$$

$$X_{\text{glycerol}} = 1 \text{ mol} / 6 \text{ mol} = 0.167$$

It's a good idea to check your math by making sure the mole fractions add up to 1:

$$x_{\text{water}} + x_{\text{glycerol}} = .833 + 0.167 = 1.000$$

**• Parts Per Million**

**Symbol:** ppm

**Definition:** It is defined as the parts of a component per million parts ( $10^6$ ) of the solution. It is widely used when a solute is present in trace quantities.

**Unit:** ppm

**Formula:**

$$\text{PPM} = \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 10^6$$

**Example:**

Calculate the molar concentration of 2000 ppm of  $\text{Pb}^{2+}$  (A. M. = 207 g/mol)?

**Solution:**

$$\text{PPM} = M \times \text{M. M.} \times 1000$$

$$M = \frac{\text{PPM}}{\text{M. M.} \times 1000} = \frac{2000}{207 \times 1000} = 0.0009 \text{ mol/L}$$

- **Molarity:**

**Symbol :** M

**Definition:** Molarity of any solution is number of moles of solute per liter of solution

**Unit:** mol/litre

**Formula:**

Molarity = Number of moles of solute / Volume of solution in liter.

$$\frac{\text{Grams}}{\text{Molar Mass}} = \text{Moles}$$

$$\frac{\text{Moles}}{\text{Volume}} = \text{Molarity}$$

**Example:**

What is the molarity of a solution containing 0.32 moles of NaCl in 3.4 liters?

**Solution:**

$$\text{Molarity} = \frac{0.32 \text{ Moles NaCl}}{3.4 \text{ L}}$$

$$= 0.94 \text{ M NaCl}$$

- **Molality**

**Symbol:** m

**Definition:** Molality of any solution is represented as the number of moles of solute present per kg of solvent

**Unit:** mol/kg

**Formula:**

Molality(m) = Number of moles of solute / Mass of solvent in Kg

**Note:** Why m is not affected by change in temperature?

Since it is dependent on mass of solute and mass do not change to small shift in temperature due to close packing of solid atoms therefore it is independent of temperature change.

$$\text{Molality (M)} = \frac{\text{Moles of Solute}}{\text{Kilograms of Solvent}}$$

**Example:**

What is the molarity of a solution containing 0.46 mole of solute in 2.0 kg water?

Given:

Moles of Solute = 0.46 mole

Kilogram of Solvent = 2.0 kg

$$\text{Molality (M)} = \frac{\text{Moles of Solute}}{\text{Kilograms of Solvent}}$$

**Solution:**

$$\text{Molality (M)} = \frac{\text{Moles of Solute}}{\text{Kilograms of Solvent}}$$

$$= \frac{0.46 \text{ mole}}{2.0 \text{ kg}}$$

= 0.23 m

- **Normality**

**Symbol :** N

**Definition:** It is defined as the gram equivalent weight per liter of solution.

**Unit:** equivalent/L

**Formula:**

**Normality = Number of grams Equivalent of solute / Volume of solution in L**

**Number of gram-equivalents of solute = Mass of solute in gram / Equivalent weight**

$$N = \frac{\text{The no. of eqv. of solute}}{\text{Volume of solution in L}}$$

We have,

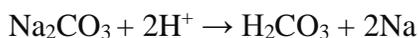
$$\text{no of g. eqv.} = \frac{\text{Mass in g}}{\text{Eqv. mass}}$$

By substitution,

$$\text{Normality} = \frac{\text{Mass of solute in g}}{\text{Eqv. mass} \times \text{Vol. of solution in L}}$$

**Example:**

Calculate the normality of 0.53 g/100 mL solution of  $\text{Na}_2\text{CO}_3$  (M.M. = 106 g/mol) as the following reaction:



**Solution:**

Eq. wt. of  $\text{Na}_2\text{CO}_3 = 106/2 = 53 \text{ g/eq}$

$$N = \frac{0.53 \text{ g}}{53 \frac{\text{g}}{\text{eq}} \times \left(100 \text{ mL} \times \frac{1\text{L}}{100 \text{ mL}}\right)} = \frac{0.53 \text{ g} \times 1000}{53 \left(\frac{\text{g}}{\text{eq}}\right) \times 100 \text{ (L)}} = 0.1 \text{ eq/L}$$

• **Formality**

**Symbol :** F

**Definition:** It is the number of formula weights of solute present per liter of the solution.

Unit: mol/L

**Formula:**

$$F = \frac{\text{Weighth of solute in gram}}{\text{Formula wt} \times \text{Volume in litre}}$$

It is applicable in case of ionic solids like NaCl.

**Example:**

Calculate the formality of solution in which 948 gram potash alum is dissolved in 5 litre solution.

**Solution:**

The formula mass of potash alum is 474 gram (formula mass)<sup>-1</sup>.

$$\begin{aligned} \text{Formality of Potash Alum (F)} &= \frac{1000 \times \text{mass of solute (gram)}}{\text{Formula mass of solute} \times \text{Volume of solution (ml)}} \\ &= \frac{1000 \times 948}{474 \times 5000} = 0.4 \text{ F} \end{aligned}$$

- **.Raoult's law**

Raoult's law states that a solvent's partial vapour pressure in a solution (or mixture) is equal or identical to the vapour pressure of the pure solvent multiplied by its mole fraction in the solution.

Mathematically, Raoult's law equation is written as;

$$P_{\text{solution}} = X_{\text{Solvent}} \cdot P^{\circ}_{\text{solvent}}$$

Where,

$P_{\text{solution}}$  = vapour pressure of the solution,

$X_{\text{solvent}}$  = mole fraction of the solvent,

$P^{\circ}_{\text{solvent}}$  = vapour pressure of the pure solvent,

Raoult's law is valid only for ideal solutions.

We will further understand the principle behind the law by looking at the example below. Consider a solution of volatile liquids A and B in a container. Because A and B are both volatile, there would be both particles of A and B in the vapour pressure. Hence, the vapour particles of both A and B exert partial pressure which contributes to the total pressure above the solution.

Raoult's law is valid only for ideal solutions.

Raoult's Law further states that at equilibrium,

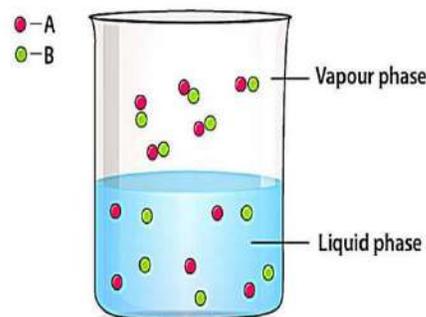
$$P_A = P^{\circ}_A \cdot X_A, \quad P_B = P^{\circ}_B \cdot X_B$$

Where  $P_A$  is the partial pressure of A.  $P^{\circ}_A$  is vapour pressure of pure A at that temperature.

$X_A$  is mole fraction of A in the liquid phase.

Where  $P_B$  is the partial pressure of B.  $P^{\circ}_B$  is vapour pressure of pure B at that temperature.

$X_B$  is mole fraction of B in the liquid phase.



### **Colligative properties:**

The colligative properties depend only upon the number of particles of the solute in the solution. They do not depend upon the nature of the solute. These properties help us in determining the relative molecular mass of a non-volatile solute. The colligative properties are :

- Relative lowering of vapour pressure,
- Elevation of boiling point,
- Depression of freezing point, and
- Osmotic pressure.

## Relative lowering of vapour pressure:

If a pure liquid is placed in a closed container that is initially evacuated, the liquid evaporates to fill up the space above the liquid. At any given temperature when equilibrium is established, the pressure exerted by the vapours of a liquid is called the vapour pressure of the pure liquid ( $P^0_1$ ). If a non-volatile solute is added to this liquid, the equilibrium vapour pressure ( $P_1$ ) over the solution is found to be less than that of the pure liquid. According to Raoult's law, the vapour pressure ( $P_1$ ) of the solvent of an ideal solution is given by

$$P_1 = P^0_1 \cdot x_1 \text{ ----- 1}$$

where  $x_1$  is the mole fraction of the solvent in the solution and  $P^0_1$  is the vapour pressure of the pure solvent. Since the solute is non-volatile, its contribution towards the vapour pressure of the solution is negligible. Hence, the vapour pressure of solution containing a non-volatile solute is only due to the solvent. Since the mole fraction ( $x_1$ ) of the solvent is less than one, it is clear that  $P_1$ , will also be less than  $P^0_1$ . The lowering of vapour pressure when a non-volatile solute is added to a solvent is given by ( $P^0_1 - P_1$ ).

Substituting for  $P_1$  in equ. 1, we get

$$P^0_1 - P_1 = P^0_1 - P^0_1 \cdot x_1 = P^0_1 (1 - x_1)$$

Since  $x_1 + x_2 = 1$ ,

$$P^0_1 - P_1 = P^0_1 \cdot x_2 \text{ ----- 2}$$

Where  $x_2$  is the mole fraction of the solute.

According to Eq. 2, the lowering of vapour pressure of the solvent depends both on the vapour pressure of the pure solvent and on the mole fraction of the solute in the solution. In other words, it depends on the nature of the solvent and on the concentration of the solute and not on the nature of the solute.

$$\frac{P^0_1 - P_1}{P^0_1} = x_2$$

The expression is called the relative lowering of vapour pressure.

"The relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute."

The above statement is also called Raoult's law of relative lowering of vapour pressure.

Now,

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1} + \frac{W_2}{M_2}} = \frac{W_2 M_1}{M_2 W_1} ; \quad \frac{W_1}{M_1} \gg \frac{W_2}{M_2}, \text{ hence } \frac{W_2}{M_2} \text{ can be neglected.}$$

Calculate the vapor pressure of a solution made by dissolving 50.0 g glucose,  $C_6H_{12}O_6$ , in 500 g of water. The vapor pressure of pure water is 47.1 torr at  $37^\circ C$

## Solution

To use Raoult's Law, we need to calculate the mole fraction of water (the solvent) in this sugar-water solution.

$$X_{\text{solvent}} = \frac{\text{moles of water}}{\text{moles of solute} + \text{moles of solvent}}$$

$$X_{\text{solvent}} = \frac{\text{moles of water}}{\text{moles of solute} + \text{moles of solvent}}$$

$$X_{\text{solvent}} = \frac{n_{\text{water}}}{n_{\text{water}} + n_{\text{glucose}}} \quad \chi_{\text{solvent}} = \frac{n_{\text{water}}}{n_{\text{water}} + n_{\text{glucose}}}$$

The molar mass of glucose is 180.2 g/mol and of water is 18 g/mol. So

$$n_{\text{water}} = \frac{500\text{g}}{18\text{g/mol}} = 27.7\text{mol} \quad n_{\text{water}} = \frac{500\text{g}}{18\text{g/mol}} = 27.7\text{mol}$$

and

$$n_{\text{glucose}} = \frac{50\text{g}}{180.2\text{g/mol}} = 0.277\text{mol} \quad n_{\text{glucose}} = \frac{50\text{g}}{180.2\text{g/mol}} = 0.277\text{mol}$$

and

$$\chi_{\text{solvent}} = \frac{27.7\text{mol}}{0.277\text{mol} + 27.7\text{mol}} = 0.99 \quad \chi_{\text{solvent}} = \frac{27.7\text{mol}}{0.277\text{mol} + 27.7\text{mol}} = 0.99$$

Note that this is still relatively dilute. The pressure of the solution is then calculated via Raoult's Law (Equation 11):

$$P_{\text{solution}} = 0.99 \times 47.1 = 46.63\text{torr}$$

## Osmotic Pressure

**Osmosis**, the process by which solvent molecules can pass through certain membranes but solute particles cannot. When two solutions of different concentration are present on either side of these membranes (called *semipermeable membranes*), there is a tendency for solvent molecules to move from the more dilute solution to the more concentrated solution until the concentrations of the two solutions are equal. This tendency is called **osmotic pressure**. External pressure can be exerted on a solution to counter the flow of solvent; the pressure required to halt the osmosis of a solvent is equal to the osmotic pressure of the solution.

Osmolarity (osmol) is a way of reporting the total number of particles in a solution to determine osmotic pressure. It is defined as the molarity of a solute times the number of particles a formula unit of the solute makes when it dissolves (represented by  $i$ ):

$$\text{Osmol} = M \times i$$

If more than one solute is present in a solution, the individual osmolarities are additive to get the total osmolarity of the solution. Solutions that have the same osmolarity have the same osmotic pressure. If solutions of differing osmolarities are present on opposite sides of a semipermeable membrane, solvent will transfer from the lower-osmolarity solution to the higher-osmolarity solution. Counter pressure exerted on the high-osmolarity solution will reduce or halt the solvent transfer. An even higher pressure can be exerted to force solvent from the high-osmolarity solution to the low-osmolarity solution, a process called **reverse osmosis**. Reverse osmosis is used to make potable water from saltwater where sources of fresh water are scarce.

Osmosis is the diffusion of a fluid through a semipermeable membrane. When a semipermeable membrane (animal bladders, skins of fruits and vegetables) separates a solution from a solvent, then only solvent molecules are able to pass through the membrane.

The osmotic pressure of a solution is the pressure difference needed to stop the flow of solvent across a semipermeable membrane. The osmotic pressure of a solution is proportional to the molar concentration of the solute particles in solution.

$$\pi = i \frac{n}{V} R.T = i.M.R.T$$

where

- $\pi$  is the osmotic pressure,
- $R$  is the ideal gas constant (0.0821 L atm / mol K),
- $T$  is the temperature in Kelvin,
- $i$  is the van 't Hoff factor

- $n$  is the number of moles of solute present,
- $V$  is the volume of the solution, and
- $M$  is the molar concentration of added solute (the  $i$  factor accounts for how many species in solution are generated)

**1. Calculate molarity of a sugar solution in water (300 K) has osmotic pressure of 3.00 atm.**

Since it is sugar, we know it doesn't dissociate in water, so  $i$  is 1. Then

$$M = \pi / RT = 3.00 \text{ atm} / (0.0821 \text{ atm}\cdot\text{L}/\text{mol}\cdot\text{K})(300 \text{ K}) = 0.122 \text{ M}$$

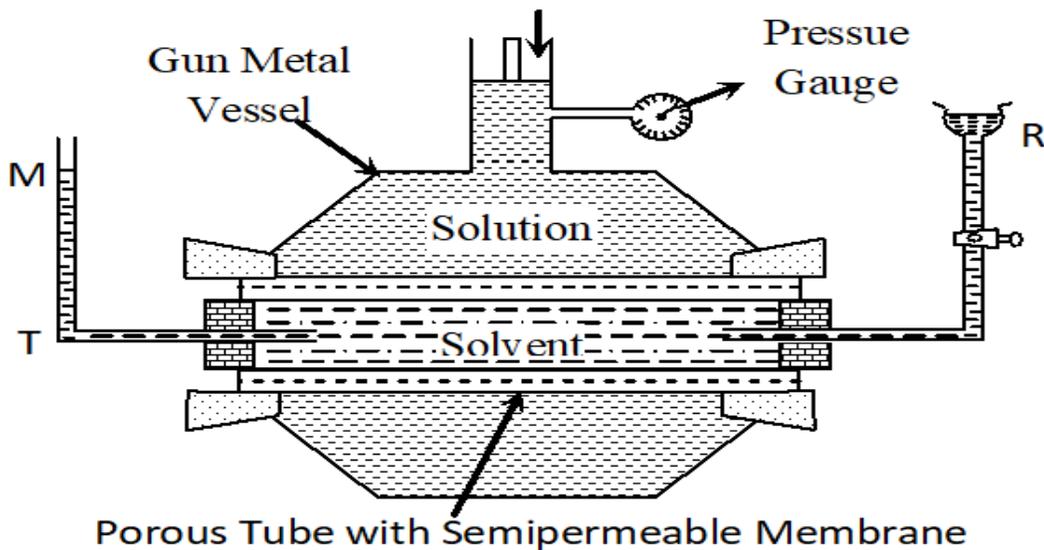
**2. Calculate osmotic pressure for 0.10 M  $\text{Na}_3\text{PO}_4$  aqueous solution at 20°C.**

Since  $\text{Na}_3\text{PO}_4$  ionizes into four particles ( $3 \text{ Na}^+ + \text{PO}_4^{3-}$ ), then  $i=4$ . We can then calculate the osmotic pressure as

$$\pi = i.M.R.T = (4).(0.10).(0.0821).(293) = 9.6 \text{ atm}$$

**Determination of Osmotic Pressure by Berkeley and Hartley's method**

Abbe Nollet (1748) was the first to observe the phenomenon of osmosis and made measurements of osmotic pressure. His measurements with a pig's bladder as the semi-permeable membrane gave only semi-quantitative results as the pig's bladder is not a good semi-permeable membrane.

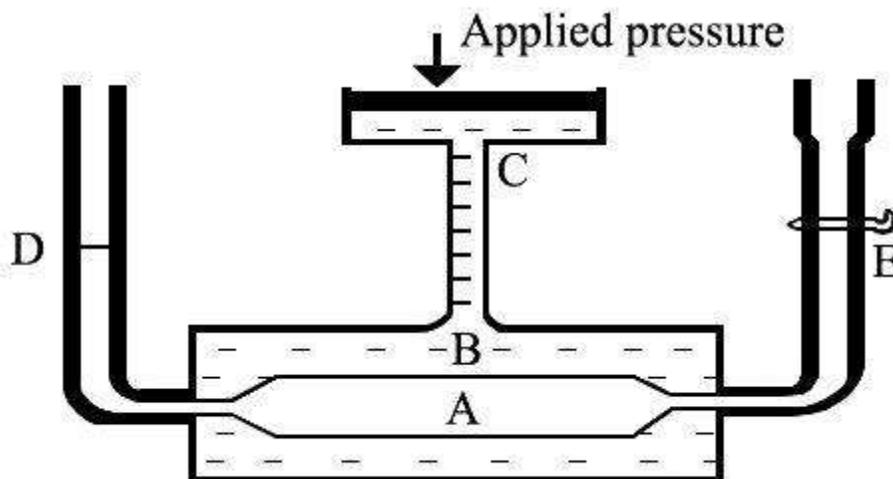


**Fig:**  
**Osmotic**

**Pressure by Berkeley and Hartley's method**

**Berkeley and Hartley's method:** The principle of the method is illustrated in Figure. The apparatus consists of two concentric cylindrical tubes, A and B. The porous tube, A, carries in it the semi-permeable membrane of copper ferrocyanide. The inner tube is surrounded in the outer tube, B. The outer tube has an opening at C

through which pressure could be applied from outside. The porous tube A has two side tubes, D and E. The solvent is added to A through E. The side tube is a capillary tube so that any small change in pressure in A could be easily detected by the movement of the liquid meniscus in the tube.



**Fig: Berkeley and Hartley's pressure apparatus**

**Measurement of Osmotic Pressure:** Different methods are in use for the measurement of osmotic pressure in the laboratory but Berkeley and Hartley's method gives the preeminent results. The apparatus consists of an absorbent pot containing copper ferrocyanide deposited in its wall (acts as a semi-permeable membrane) and fixed into a bronze cylinder to which is fixed a piston and a pressure determine (to read the applied pressure).

**Procedure** – The porcelain tube is filled with pure solvent and the metallic jacket with a solution. The level in the capillary tube will tend to move down as the solvent flows towards solution due to osmosis. External pressure is now applied on the solution by the piston so that level in capillary remains stationary. The reading of pressure gauge is recorded. This is the osmotic pressure of the solution.

The pot is fixed with a tube indicator on left and water reservoir on right. Pot is filled with water while the cylinder is filled with a solution whose osmotic pressure is to be measured. Water tends to pass into the solution through the semipermeable membrane with the result that the water level in the indicator falls down. External pressure is now applied with the piston so as to preserve a constant level in the indicator. This external pressure is osmotic pressure.

## Elevation in Boiling Point

Water boils at 100°C at 1atm of pressure, but a solution of salt water does not. When table salt is added to water, the resulting solution has a higher boiling point than the water itself. The ions form an attraction with the solvent particles that prevents the water molecules from going into the gas phase. Therefore, the saltwater solution will not boil at 100°C. In order for the saltwater solution to boil, the temperature must be raised above 100°C. This is true for any solute added to a solvent; the boiling point will be higher than the boiling point of the pure solvent (without the solute). In other words, when anything is dissolved in water, the solution will boil at a higher temperature than pure water would.

The boiling point elevation due to the presence of a solute is also a colligative property. That is, the amount of change in the boiling point is related to the number of particles of solute in a solution and is not related to the chemical composition of the solute. A 0.20m solution of table salt and a 0.20m solution of hydrochloric acid would have the same effect on the boiling point.

Thus, the boiling point of a solution is higher than the boiling point of a pure solvent. However, the amount to which the boiling point increases depends on the amount of solute that is added to the solvent. A mathematical equation is used to calculate the boiling point elevation,

$$\Delta T_b = k_b \cdot m \cdot i$$

Where:

- $\Delta T_b$  = the amount the boiling point increases.
- $K_b$  = the boiling point elevation constant which depends on the solvent (for water, this number is 0.515°C/m).
- $m$  = the molality of the solution.
- $i$  = the number of particles formed when that compound dissolves (for covalent compounds, this number is always 1).

Now, 
$$m = \frac{\text{mole of solute}}{\text{solvent in kg}} = \frac{\text{mass of solute/molar mass}}{\text{solvent in kg}} = \frac{w_2}{M_2} \times \frac{1}{\text{solvent in kg}} = \frac{w_2}{M_2} \times \frac{1000}{W_1}$$

Where:

$W_2$  = weight of solute in grams.

$M_2$  = Molar mass of solute in grams.

$W_1$  = weight of solvent in grams.

$$\Delta T_b = k_b \cdot m \cdot i$$

$$\Delta T_b = i \cdot K_b \cdot \frac{w_2}{M_2} \times \frac{1000}{W_1}$$

### Depression in Freezing Point

The effect of adding a solute to a solvent has the opposite effect on the freezing point of a solution as it does on the boiling point. A solution will have a lower freezing point than a pure solvent. The freezing point is the temperature at which the liquid changes to a solid. At a given temperature, if a substance is added to a solvent (such as water), the solute-solvent interactions prevent the solvent from going into the solid phase. The solute-solvent interactions require the temperature to decrease further in order to solidify the solution. A common example is found when salt is used on icy roadways. Salt is put on roads so that the water on the roads will not freeze at the normal 0°C but at a lower temperature, as low as -9°C. The de-icing of planes is another common example of freezing point depression in action. A number of solutions are used, but commonly a solution such as ethylene glycol, or a less toxic monopropylene glycol, is used to de-ice an aircraft. The aircrafts are sprayed with the solution when the temperature is predicted to drop below the freezing point.

The **freezing point depression** is the difference in the freezing points of the solution from the pure solvent. This is true for any solute added to a solvent. The freezing point of the solution will be lower than the freezing point of the pure solvent

The freezing point depression due to the presence of a solute is also a colligative property. That is, the amount of change in the freezing point is related to the number of particles of solute in a solution and is not related to the chemical composition of the solute. A 0.20m solution of table salt and a 0.20m solution of hydrochloric acid would have the same effect on the freezing point.

The following equation is used to calculate the decrease in the freezing point:

$$\Delta T_f = k_f \cdot m \cdot i$$

Where:

- $\Delta T_f$  = the amount the freezing temperature decreases.
- $K_f$  = the freezing point depression constant which depends on the solvent (for water, this number is 1.86°C/m).

- $m$  = the molality of the solution.
- $i$  = the number of particles formed when that compound dissolves (for covalent compounds, this number is always 1).

$$\text{Now, } m = \frac{\text{mole of solute}}{\text{solvent in kg}} = \frac{\text{mass of solute/molar mass}}{\text{solvent in kg}} = \frac{w_2}{M_2} \times \frac{1}{\text{solvent in kg}} = \frac{w_2}{M_2} \times \frac{1000}{W_1}$$

Where:

$W_2$  = weight of solute in grams.

$M_2$  = Molar mass of solute in grams.

$W_1$  = weight of solvent in grams.

$$\Delta T_b = k_b \cdot m \cdot i$$

$$\Delta T_b = i \cdot K_b \cdot \frac{w_2}{M_2} \times \frac{1000}{W_1}$$

### Van't Hoff Factor:

Colligative properties such as the relative lowering of vapour pressure, Depression in Freezing point, Elevation in boiling point, and Osmotic pressure of a solution depends on the number of solute particles dissolved in the solvent. These properties are independent of the type of solute.

When a solute (ionic or covalent) is dissolved in a solvent (polar or non-polar), it undergoes dissociation or association, which affects the molar mass of the solute in the solution.

Ionic or polar compounds, on dissolution, dissociate into their corresponding cations and anions. For example, there will be 1 mole of  $\text{Cl}^-$  ions and 1 mole of  $\text{K}^+$  ions in the resulting solution (a total of 2 moles of ions in the solution) if we dissolve one mole of  $\text{KCl}$  (74.5 g) in 1 kg of water. Calculating the molar mass using the colligative properties for such solutes, it is found that the experimentally determined molar mass is always lower than its original molar mass.

On the other hand, few substances tend to associate in an aqueous state. The actual number of molecules for such solutes is always more than the number of ions/molecules present in the solution. Calculating the molar mass using the colligative properties for such solutes, it is found that the experimentally determined molar mass is always more than the true value.

The equations derived for measuring the colligative property are for non-electrolytes that do not undergo association or dissociation in any solution. The discrepancy in molar mass, also known as Abnormal Molar mass, arises either due to association or dissociation of solute particles.

Abnormal molar mass is the molar mass of the solution which is either lower or higher than the expected or normal value.

To account for the extent of dissociation or association of solute particles in a solution, van't Hoff introduced a factor (i) in 1880, known as the van't Hoff factor. The Van't Hoff factor 'i' is defined as:

$$i = \frac{\text{Normal Molar Mass}}{\text{Abnormal Molar Mass}} \quad \dots\dots\dots 1$$

$$i = \frac{\text{Observed Colligative Property}}{\text{Calculated Colligative Property}} \quad \dots\dots\dots 2$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}} \quad \dots\dots\dots 3$$

The abnormal molar mass in Equation (1) is the experimentally determined molar mass. The calculated colligative properties in Equation (2) are obtained by assuming that the non-volatile solute is neither associated nor dissociated.

A solute or electrolyte never dissociates or associates completely when dissolved in a solvent, but only up to a fraction known as the degree of dissociation which is expressed by the symbol ' $\alpha$ '.

### Van't Hoff Factor and Dissociation of Solute Molecules

Van't off factor is used to calculate the extent of dissociation of an ionic solute in terms of the degree of dissociation  $\alpha$ .

The degree of dissociation or  $\alpha$  is defined as the fraction of the total ionic solute present in the solution that undergoes dissociation into cations and anions.

$$\alpha = \frac{\text{Number of moles of the solute dissociated}}{\text{Total number of moles of the solute present in the solution}}$$

Suppose 1 mole of an electrolyte dissociates to give n number of ions, with a degree of dissociation  $\alpha$ .

At equilibrium:

Number of moles of undissociated solute left (after dissociation) =  $1 - \alpha$

Number of moles of ions formed (after dissociation) =  $n\alpha$

Total number of moles of particles (after dissociation) =  $1 - \alpha + n\alpha$

From Van't Hoff factor definition and using Eqn (3), we have:

$$i = \frac{\text{Total number of moles of particles after dissociation}}{\text{Number of moles of particles before dissociation}} = \frac{1 - \alpha + n\alpha}{1} = \frac{1 - \alpha(n-1)}{1}$$

$$i - 1 = \alpha(n-1)$$

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

The value of  $\alpha$  can be calculated by knowing the value of Van't Hoff factor ( $i$ ) from observed molar mass and normal molar mass.

### Van't Hoff Factor and Association of Solute Molecules

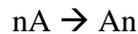
Generally, non-polar solutes undergo association to form bigger molecules. For example, ethanoic acid (acetic acid) self-associates in benzene and forms dimers.

Van't Hoff factor can be used to calculate the extent of association of a non-polar solute in terms of the degree of association ( $\alpha$ ).

The degree of association is defined as the fraction of the total non-polar solute present in the solution that undergoes association.

$$\alpha = \frac{\text{Number of moles of the solute dissociated}}{\text{Total number of moles of the solute present in the solution}}$$

Suppose we have 11 mole of the solute which undergoes association as shown:



Let the degree of association be  $\alpha$

At equilibrium:

Number of moles of unassociated solute left after association =  $1 - \alpha$

Number of moles of associated molecules formed after association =  $\alpha/n$

Total number of moles of particles after association =  $1 - \alpha + \alpha/n = 1 - \alpha + \alpha/n$

From Van't Hoff factor definition and using Eqn(3), we have:

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}} = \frac{1 - \alpha + \alpha/n}{1}$$

$$\Rightarrow i = 1 - \alpha + \alpha/n$$

$$\Rightarrow i = 1 - \alpha + \alpha/n$$

$$\Rightarrow i - 1 + \alpha = \alpha/n$$

$$\Rightarrow ni - n + \alpha n = \alpha$$

$$\Rightarrow ni - n = \alpha - \alpha n$$

$$\Rightarrow n(i-1) = \alpha(1-n)$$

$$\Rightarrow \alpha = \frac{n(i-1)}{1-n}$$

The value of  $\alpha$  can be calculated by knowing the value of observed molar mass, normal molar mass, and the number ( $n$ ) of simple molecules that undergo association.