

## Unit- 1

**SOLUTIONS**# Introduction :->

A solution is a homogenous mixture of two or more substances, whose composition can vary within certain limits.

→ In a solution, the particles of the substance are molecular or ionic level, so small that they cannot be seen with naked eyes and do not scatter light.

Example :->

- Sugar + water = sugar solution
- Salt + water = saline solution.

→ In every solution there are two main components:

1. SOLVENT: The component present in larger amount. It determines the physical state of the solution (solid, liquid or gas).

2. SOLUTE: The component present in smaller amount. It is the substance that gets dissolved in the solvent.

# Types of solutions :->

Solutions can be classified in two main ways :->

1. Based on the Number of Components —

- Binary solution: contains two components [one solute + one solvent].  
Ex → Salt in water.

- Tertiary solution: Contains three components.  
Ex  $\rightarrow$  Alcohol + Water + Acetone.
- Quaternary solution: contains more than three substances.

## 2. Based on the physical state of solvent —

### • Gaseous Solutions : $\rightarrow$

- The solvent is a gas.
- The solute can be a gas, liquid or solid.
- These are always homogenous mixtures.

★ NOTE :  $\rightarrow$  All gaseous solutions exist in the gaseous state and are uniform throughout.

### • Liquid solutions : $\rightarrow$

- The solvent is a liquid.
- These are the most common types of solutions in daily life.
- The solute can be a gas, liquid or solid.

### • Solid solutions —

- The solvent is a solid.
- These are mostly metallic mixtures (alloys) or other solid combinations.
- The solute may be a gas, liquid or solid.

• Summary Table of 9 different types of solutions —

| Types of solution   | solvent | solute                 | Example                                               |
|---------------------|---------|------------------------|-------------------------------------------------------|
| 1. Gaseous solution | Gas     | Gas<br>Liquid<br>Solid | Air ( $O_2 + N_2$ )<br>Moist air<br>Smoke             |
| 2. Liquid solution  | Liquid  | Gas<br>Liquid<br>Solid | Soda water<br>Alcohol in water<br>salt/sugar in water |
| 3. Solid solution   | Solid   | Gas<br>Liquid<br>Solid | Hydrogen in Palladi<br>Amalgam<br>Brass (Copper+Zn)   |

# Determination of concentration of the solution :→

The concentration of a solution tells us how much solute is present in a given quantity of solvent or solution.

It can be expressed in several ways depending on the requirement.

1. Mass percentage (W/W %): The mass of solute present in 100 g of solution.

$$\text{Mass percentage} = \frac{\text{Amount of solute (in g)}}{\text{Amount of solution (in g)}} \times 100$$

$$= \frac{\text{Amount of solute (in g)}}{\text{Amount of solute (g)} + \text{Amount of solvent (g)}} \times 100$$

→ General formula,

$$\therefore \% \text{ w/w} = \frac{W_B}{W_B + W_A} \times 100$$

Where, A is solvent and B is solute.

Example → 10 g NaCl in 90 g water ⇒ 10% w/w.

Q. If we have 10 molal urea solution calculate Mole fraction of urea in this solution & also calculate % w/w of urea. (MW = 60 gm)

Ans. 10 moles urea in 1000 gm of water

$$X_{\text{urea}} = \frac{10}{10 + \frac{1000}{18}} = \frac{10}{65.55}$$

$$\begin{aligned} \% \text{ w/w weight of urea} &= \frac{10 \times 60}{10 \times 60 + 1000} \times 100\% \\ &= 37.5\% \end{aligned}$$

2. Volume percentage (V/V %): The volume of solute present in 100 ml of solution.

$$\text{Volume percentage} = \frac{\text{Volume of solute (in mL)}}{\text{Volume of solution (in mL)}} \times 100$$

$$= \frac{\text{Volume of solute (in mL)}}{\text{Volume of solute (mL)} + \text{Volume of solvent (mL)}} \times 100$$

→ General formula,

$$\% \text{ v/v} = \frac{V_B}{V_A + V_B} \times 100$$

Where,  $V_B$  = Volume of solute  
 $V_A$  = Volume of solvent.

**Example**  $\rightarrow$  40 mL alcohol in 100 mL solution  $\rightarrow$   
 volume % = 40 %.

3. Mass/volume percentage (W/V%) : The mass of solute present in 100 mL of solution.

$$\text{Mass-volume percentage} = \frac{\text{Amount of solute (in g)}}{\text{Amount of solution (in mL)}} \times 100$$

**Example**  $\rightarrow$  5g NaCl in 100 mL water  $\rightarrow$  5% W/V.

4. Parts per million (PPM) : When a solute is present in very minute amounts. Its conc. is expressed in PPM.

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

5. Normality (N) : Number of equivalents of solute per litre of solution.

$$\text{Normality (N)} = \frac{\text{gram equivalents of solute}}{\text{volume of solution in Ltr.}}$$

**Example**  $\rightarrow$  Equivalent strength of solute in 1L solution.

Q.  $2.5 \text{ cm}^3$  of  $0.2 \text{ M H}_2\text{SO}_4$  solution is diluted to  $0.5 \text{ dm}^3$ . Find normality of the diluted solution:

a.  $0.2 \text{ N}$

b.  $0.02 \text{ N}$

c.  $0.002 \text{ N}$

d.  $0.04 \text{ N}$

$$\text{Ans. (c)} \quad V_1 = 2.5 \text{ cm}^3 = 2.5 \times 10^{-3} \text{ dm}^3$$

$$M_1 = 0.2 \text{ M}$$

$$N_1 = 2 \times M_1 = 0.4 \text{ N}$$

$$V_2 = 0.5 \text{ dm}^3$$

$$N_1 V_1 = N_2 V_2$$

$$0.4 \times 2.5 \times 10^{-3} = N_2 \times 0.5$$

$$N_2 = 2 \times 10^{-3} = 0.002 \text{ N}$$

6. Molarity (M): Number of moles of solute per litre of solution.

$$M = \frac{\text{moles of solute}}{\text{volume of solution in l}}$$

Example → Moles of solute in 1 L of solution.

\* Both normality and molarity of a solution change with change in temperature.

7. Molality (m): Number of moles of solute per kg of solvent.

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

Example → Moles of solute in 1 kg of solvent (doesn't depend on temperature).

\* A solution having molarity equal to 1 unit is called "molar solution".

\* A solution containing one mole of solute per 1000 gm of solvent has molality equal to 1, and is called a "molal solution".

Relation b/w Molarity & molality :

$$m = \frac{1000 \times \text{Molarity}}{1000 \times \text{density} - \text{Molar mass} \cdot \text{Molarity}}$$

→ Dilution formula: If the solution of same substance is diluted by adding solvent from volume  $V_1$  to volume  $V_2$  then initial molarity  $M_1$  and final molarity  $M_2$  are related as —

$$[M_1 V_1 = M_2 V_2]$$

### # Solubility of Gases in Liquids :→

solubility of a gas in a liquid is the maximum amount of gas that can dissolve in a certain quantity of liquid at a specific temperature and pressure.

It forms a saturated solution when no more gas can dissolve.

### \* Factors affecting solubility of gases in liquids —

#### 1. Effect of pressure (Henry's Law) :→

- Observation: Gas solubility increases if the pressure of the gas above the liquid increases.
- Reason: More gas molecules are "pushed" into the liquid at higher pressure.
- Law:  $C \propto P$  or  $C = K_H \cdot P$   
 Where,  $K$  = Henry constant.  
 $C$  = solubility of the gas (mol/L)  
 $P$  = partial pressure of the gas above the liquid

### Application of Henry's law

- ▶ Sea divers use air diluted with He (11.7% He, 56.2%  $N_2$  and 32.1%  $O_2$ ) to avoid a condition known as 'bends' to cope up with high 'P' under water.
- ▶ At high altitudes, when partial pressure of  $O_2$  is less, it leads to a condition known as 'Anoxia'. They should carry  $O_2$ .

**\* Key points :->**

#### (A) Direct Proportionality :

- If pressure doubles, solubility doubles.
- If pressure halves, solubility halves.

#### (B) Temperature Dependence :

- $K_H$  increases with increase in temperature, so solubility of gases decreases at higher temperature

Q. If  $K_H = 0.034 \text{ (mol/L} \cdot \text{atm)}$  for  $O_2$  at  $25^\circ\text{C}$  and the partial pressure of  $O_2$  is  $0.21 \text{ atm}$ :

$$\rightarrow C = K_H \cdot P = 0.034 \times 0.21 = 0.00714 \text{ mol/L.}$$

#### # Limitations of Henry Law :->

- (a) Pressure is not very high.
- (b) Not applicable if gas reacts chemically with the solvent (eg.  $CO_2 + H_2O \longrightarrow H_2CO_3$ ).
- (c) May fail at high gas concentrations (solution near saturation).
- (d) Law is valid only at constant temperature; solubility decreases as temperature rises.

## 2. Effect of Temperature :→

- Observation : Solubility of gases decreases with increase in temperature.
- Reason : Gas molecules gain kinetic energy → escape from the solution.
- Example :
  - Warm soda fizzes more.
  - Oxygen dissolves less in warm water → aquatic life needs cooler water.

## 3. Nature of solvent :→

- Effect : Polar solvents dissolve polar gases better; non-polar solvents dissolve non-polar gases better.
- Example : Water (polar) dissolves  $\text{NH}_3$  better than  $\text{O}_2$ .

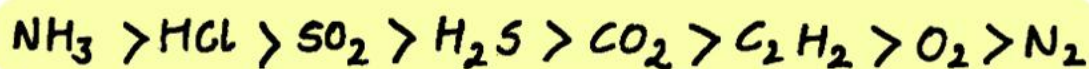
## ★ Trick to Remember :→

"Pressure Pushes, Heat escapes, Polarity Helps".

## 4. Nature of gas :→

Polar gases dissolve easily in polar liquids; non-polar gases dissolve less.

The decreasing order of absorption coefficient of various gases in 1 mL water is given below :



→  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$  are more soluble in ethyl alcohol than water.

→  $O_2$  is readily soluble in blood.

## # SOLID SOLUTIONS :-→

A solid solution is a homogenous mixture of two or more solids where the solute is uniformly distributed in the solid solvent.

### → Types of solid solutions :-→

#### 1. Substitutional solid solution —

- some atoms of the solvent are replaced by solute atoms of similar size.

##### • Example :

- Brass → Cu + Zn
- Bronze → Cu + Sn

#### 2. Interstitial solid solutions —

- small solute atoms fit into the empty spaces between solvent atoms.

##### • Example :

- steel → C in Fe
- Hydrogen-Palladium alloy → H in Pd.

### → Characteristics :→

- Homogeneous at the atomic level.
- Cannot be separated by physical means.
- Usually stronger and more corrosion-resistant than pure metals.

### # Vapour Pressure of Liquids Solutions :→

When a liquid is kept in a closed container, some molecules escape from its surface and form vapours.

- The pressure exerted by these vapours on the liquid surface is called "vapour pressure".
- When two or more liquids are mixed, the total vapour pressure of the solution depends on the nature and amount of each component.
- The process by which the molecules of vapours are mixed at the surface of liquid i.e. change of vapour to liquid state is known as condensation.
- Evaporation and condensation are opposite reactions of each other. When the rate of evaporation is equal to the rate of condensation, then the equilibrium is established.

### → Types of Liquid solutions :→

There are two main types —

#### (a) Ideal solutions :

- Obey Raoult's Law at all concentrations.
- The Forces between A-A, B-B and A-B molecules are similar.
- No heat is absorbed or evolved on mixing.
- Example : Benzene + Toluene, n-Hexane + n-Heptane

#### (b) Non-ideal solutions :

- Do not obey Raoult's Law.
- Forces between A-B are different from A-A or B-B.
- They show deviation from Raoult's Law.

### → Graph :→

- For ideal solutions → vapour pressure vs mole fraction is straight line.
- For non-ideal solutions → curve above or below the straight line (depending on deviation).

### → RAOULT'S LAW :→

The partial vapour pressure of each component in a solution is directly proportional to its mole fraction in the liquid phase.

### • Mathematical Form :

For a binary solution of liquids A and B.

$$P_B = P^{\circ} X_B$$

where:

- vapour pressure of pure A and B
- mole fractions
- partial vapour pressures.

### → Important Points :

- Raoult's Law is applicable only for ideal solutions.
- It forms the basis for understanding vapour-liquid equilibrium.
- It can be combined with Dalton's Law of Partial Pressures for gas phase analysis.

### → Limitations :

1. Not applicable to non-ideal solutions.
2. Valid only when solute and solvent are chemically similar.
3. Fails for electrolytes or strongly associated/dissociated substances.

### → Example :

- Benzene + Toluene (ideal, obeys Raoult's Law).
- Acetone + chloroform (non-ideal, negative deviation).

# Vapour pressure of solutions of solids in liquids :->

When a non-volatile solid (like salt or sugar) is dissolved in a volatile solvent (like water), the vapour pressure of the solvent decreases.

This happens because solute particles occupy space on the surface, reducing the number of solvent molecules that can escape into vapour form.

-> Explanation :

- Pure solvent → all surface particles are solvent → high vapour pressure.
- Solution → some surface sites are occupied by solute → fewer solvent particles escape → lower vapour pressure

This phenomenon is called vapour pressure lowering

-> Raoult's Law for solute in solvent :->

$$\frac{P_0 - P}{P_0} = X_{\text{solute}}$$

where:

- $P_0$  = vapour pressure of pure solvent.
- $P$  = vapour pressure of solution
- $X_{\text{solute}}$  = mole fraction of solute.

It shows that relative lowering of vapour pressure is equal to the mole fraction of solute.

**Ques. 1]** State Raoult's Law for the solution containing volatile components. What is the similarity between Raoult's Law and Henry Law?

**Ans.]** Raoult's Law states that the partial pressure of the vapour of a volatile component in a solution is directly proportional to its mole fraction in the solution.

Raoult's Law is a special case of Henry's Law. Both Henry's Law and Raoult's Law describe the relationship between a solution and its vapour that is in equilibrium with each other.

**Q. 2** Why does adding salt to water lower its vapour pressure?

**Ans.]** When salt ( $\text{NaCl}$ ) is added to water, it dissociates into ions ( $\text{Na}^+$  and  $\text{Cl}^-$ ).

These ions attract water molecules around them, reducing the number of water molecules that can escape into vapour form.

As a result, the vapour pressure of the solution becomes lower than that of pure water.

### # Ideal solution :→

An ideal solution is one that obeys Raoult's Law completely at all concentrations and temperatures.

#### That means :

The partial vapour pressure of each component is directly proportional to its mole fraction in the solution.

$$P_A = P_A^\circ \times X_A$$

$$P_B = P_B^\circ \times X_B$$

$$P_{\text{total}} = P_A + P_B$$

### • Characteristics of Ideal Solutions :→

1. Raoult's law holds for both components at all compositions.
2. No enthalpy change on mixing :

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

3. No volume change on mixing :  $\Delta V_{\text{mix}} = 0$

4. Intermolecular forces between A-A, B-B and A-B are similar.

### → Examples :→

- Benzene + Toluene
- Hexane + Heptane
- Ethyl chloride + Ethyl Bromide
- n-Butane + n-Pentane
- $\text{CCl}_4$  +  $\text{SiCl}_4$ .

These pairs have similar size and polarity, so mixing doesn't disturb molecular forces much.

### # Non-Ideal Solutions :→

A non-ideal solution is one that does not obey Raoult's law at all concentrations or temperatures.

In these solutions, the interactions between A-B molecules are different from A-A or B-B.

### → Types of Non-ideal solutions :→

Non-ideal solutions are of two types—

#### (a) Positive Deviation from Raoult's Law :

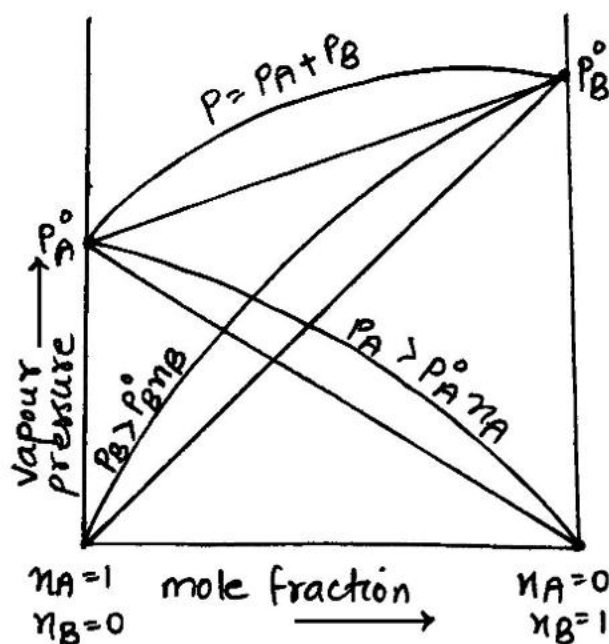
- When A-B attraction  $<$  A-A or B-B attraction
- Molecules escape more easily  $\rightarrow$  vapour pressure increases
- Mixing is endothermic (absorbs heat).

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

#### → Examples :→

- Ethanol + Acetone
- Carbon tetrachloride + Toluene
- Acetone + Benzene
- Methanol + Water.

Fig:→ Vapour pressure curve showing (+ve) deviation from Raoult's Law.



#### (b) Negative Deviation from Raoult's Law :

- When A-B attraction  $>$  A-A or B-B attraction.
- Fewer molecules escape  $\rightarrow$  vapour pressure decreases.

- Mixing is exothermic (releases heat).

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

→ Examples :→

- Chloroform + Acetone.
- Phenol + Aniline.
- Acetone + chloroform.

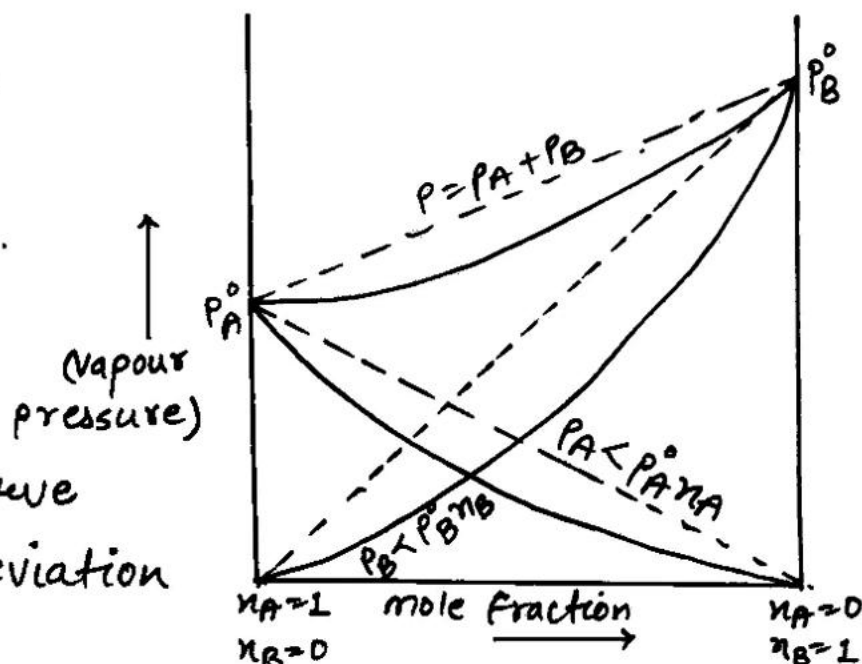


Fig - Vapour pressure curve showing negative deviation from Raoult's law.

**Q.** If two components A and B have  $P_A^0 : P_B^0 = 1 : 2$  and have mole fraction in solution 1 : 2 then mole fraction of A in vapour is:

- 0.33
- 0.25
- 0.52
- 0.2

**Ans. (d)** Mole fraction of component 'A' in vapour phase

$$= \frac{\text{Partial pressure of 'A'}}{\text{Total Vapour pressure}} = \frac{P_A}{P_A + P_B}$$

$$\text{but; } P_A = P_A^0 x_A$$

$$P_B = P_B^0 x_B = \frac{P_A^0 x_A}{P_A^0 x_A + P_B^0 x_B}$$

$$P_A^0 = 1, x_A = 1, P_B^0 = 2, x_B = 2$$

## Azeotropic Mixture or Constant Boiling Mixture

Mixture of two or more components that is like a pure chemical compound boils and distills over completely at the same temperature without change in composition is called an azeotrope. Non ideal solutions form azeotropes.

There are two types of azeotropes:

### Azeotropic mixture with minimum Boiling point

→ Formed by liquids showing positive deviation. An intermediate composition of liquids having highest vapour pressure, thus lowest boiling point gives this azeotrope. Such azeotropes have boiling points lower than either of the pure component.

#### Examples:

- Acetone +  $C_2H_5OH$  (ethyl alcohol or ethanol)
- $CCl_4$  (carbon tetrachloride) +  $CHCl_3$  (chloroform)
- Acetone + Benzene

### Azeotropic mixture with maximum boiling point

→ It is formed by liquids showing negative deviation. An intermediate composition of liquids having minimum vapour pressure, thus highest boiling point gives this azeotrope. Such azeotropes have boiling points higher than either of the pure components.

#### Examples:

- Acetone + Aniline
- $HCl$  + water
- $HNO_3$  (68%) + water (32%) non-ideal mixture boiling at 395.5 K
- $H_2SO_4$  + water

## # Colligative Properties and Determination of Molar Mass-

### → Introduction:

When a non-volatile solute (like sugar or urea) is dissolved in a pure solvent (like water or benzene), certain physical properties of the solvent change. These changes depend only on the number of solute particles present and not their chemical nature.

Such properties are called colligative properties.

### • Definition:

Colligative properties are those properties of a solution that depend only on the number of solute particles and not on the nature of the solute.

### ◆ Types of colligative properties: →

There are four main colligative properties:

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

## # Relative Lowering of vapour pressure—

### • Concept: →

When a non-volatile solute is added, the vapour pressure of the solvent decreases. This happens because some surface molecules of the solvent are replaced by solute molecules, which cannot escape into vapour form.

• Raoult's Law (for dilute solutions):

$$\frac{P^{\circ} - P}{P^{\circ}} = X_{\text{solute}}$$

or if solution is very dilute,

$$\frac{P^{\circ} - P}{P^{\circ}} = \frac{n_2}{n_1}$$

where:

$P^{\circ}$  = vapour pressure of pure solvent  
 $P$  = vapour pressure of solution  
 $X_{\text{solute}}$  = Mole fraction of solute.

• Explanation :→

Adding solute particles lowers the vapour pressure, because fewer solvent molecules can escape. This lowering is proportional to the number of solute particles (moles of solute).

→ It is used to calculate molar mass of solute experimentally.

# Elevation in Boiling point —

• Concept :→

The boiling of a liquid is the temperature at which its vapour pressure becomes equal to external atmospheric pressure.

When solute is added:

- vapour pressure of solvent decreases.
- Hence, a higher temperature is required to reach the same vapour pressure → boiling point rises.

→ Formula,

$$\Delta T_b = K_b \times m$$

Where:

- $\Delta T_b$  = Elevation in boiling point
- $K_b$  = Ebullioscopic constant (depends on solvent).
- $m$  = Molality of solution.

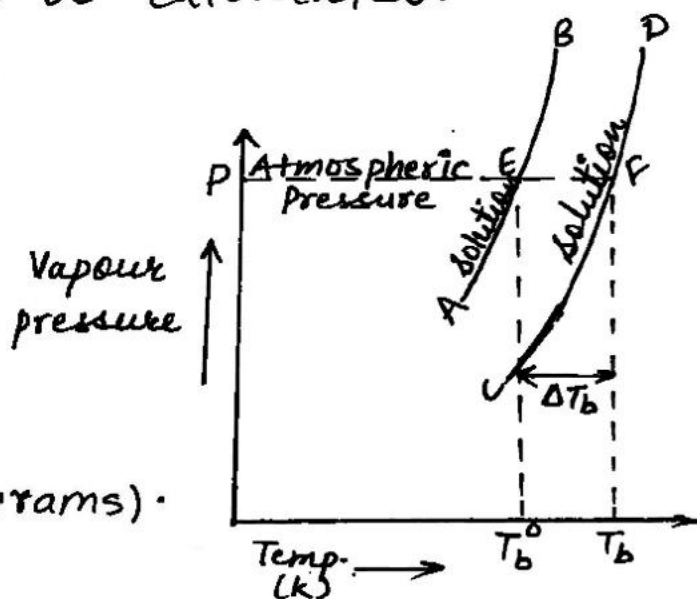
→ Explanation:

This increase is directly proportional to the molality (moles of solute per kg solvent). Thus, by measuring the rise in boiling point, the molar mass of solute can be calculated.

→ Formula for molar mass:

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

Where:

 $w_2$  = mass of solute $w_1$  = mass of solvent (in grams).# Depression in Freezing Point —• Concept:

The freezing point of a liquid is the temperature at which the liquid and solid phases are in equilibrium.

When a solute is added:

- Solute particles prevent solvent molecules from forming solid crystals easily.

- Therefore, freezing point decreases.

→ Formula :→

$$\Delta T_f = K_f \times m$$

where:

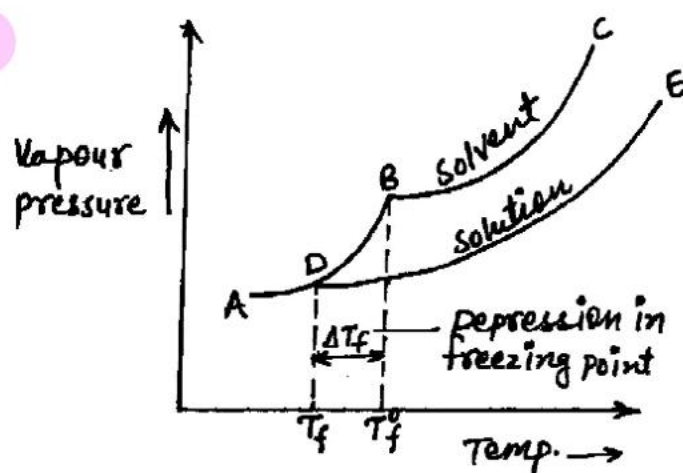
- $\Delta T_f$  = Depression in freezing point
- $K_f$  = Cryoscopic constant (depends on solvent)
- $m$  = Molality of solution.

→ Explanation:

The greater the number of solute particles the greater the lowering of freezing point. This is also used to find molar mass of solute.

→ Formula for molar mass:

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$



- Q. The depression in freezing point is found to be 0.68 K on dissolving 25.6 g sulphur in 1000 g naphthalene. Determine the molecular formula of sulfur. ( $K_f$  for naphthalene =  $6.8 \text{ K kg mol}^{-1}$ ).

Ans-

$$M_B = \frac{K_f}{\Delta T_f} \times \frac{W_B}{W_A} \times 1000$$

Given,  $K_f = 6.8 \text{ K kg mol}^{-1}$

$\Delta T_f = 0.68 \text{ K}$

$W_B = 25.6 \text{ g}$

$W_A = 1000 \text{ g}$

$$M_B = \frac{6.8}{0.68} \times \frac{25.6}{1000} \times 1000$$

$$M_B = 256$$

→ Let the molecular formula of sulphur in  $S_n$  —

$$\therefore \text{Molecular weight} = n \times 32$$

$$n \times 32 = 256$$

$$n = \frac{256}{32} = 8$$

$\therefore$  The molecular formula of sulphur is  $S_8$ .

**Q.** Calculate the freezing point of a solution of a non-volatile solute in a unknown solvent of molar mass 30 g/mole having mole fraction of solvent equal to 0.8. Given that latent heat of fusion of solid solvent =  $2.7 \text{ kcal mol}^{-1}$ , freezing point of solvent =  $27^\circ\text{C}$  and  $R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$ .

**Ans.**

$$\therefore K_f = \frac{MRT^2}{1000 \Delta H_f} = \frac{2 \times 300 \times 300 \times 30}{1000 \times 2700} = 2.00 \text{ K kg mol}^{-1}$$

$$\text{mole fraction of water} = 0.8$$

$$\therefore \text{mole fraction of solute} = 0.2$$

$$\text{or } 0.2 = \frac{n}{n+N} \text{ and } 0.8 = \frac{N}{n+N}$$

$$\therefore \frac{n}{N} = \frac{0.2}{0.8} = \frac{1}{4} = \frac{wM}{mW}$$

$$\text{or } \frac{1}{4} = \frac{w \times 30}{mW} \quad \therefore \frac{w}{mW} = \frac{1}{4 \times 30}$$

$$\therefore \Delta T_f = \frac{100 \times w \times K_f}{m \times W} = \frac{1000 \times 2.0}{4 \times 30} = 16.67$$

$$\text{F.P of solution} = 10.33^\circ\text{C}$$

# Diffusion :→ When potassium permanganate added in container of water then after some time violet colour spreads in container. The process in which the movement of molecules takes place from high conc area to low concentration area is known as diffusion.

# Osmosis :→ When thistle funnel having semi-permeable membrane filled with coloured solution of sugar is hanging in a container of water, then thistle funnel allows to pass molecules of solvent through it, but does not allow the molecules of solute.

The process of passing of solvent molecules from the solution of lower concentration to solution of higher concentration through a semi-permeable membrane is called osmosis.

- semi-permeable membrane is made up of chemical substance phenol or potassium ferriocyanide.
- semi-permeable membrane is like a continuous sheet which contains a network of very small pores which allow to pass molecules of solvent only.

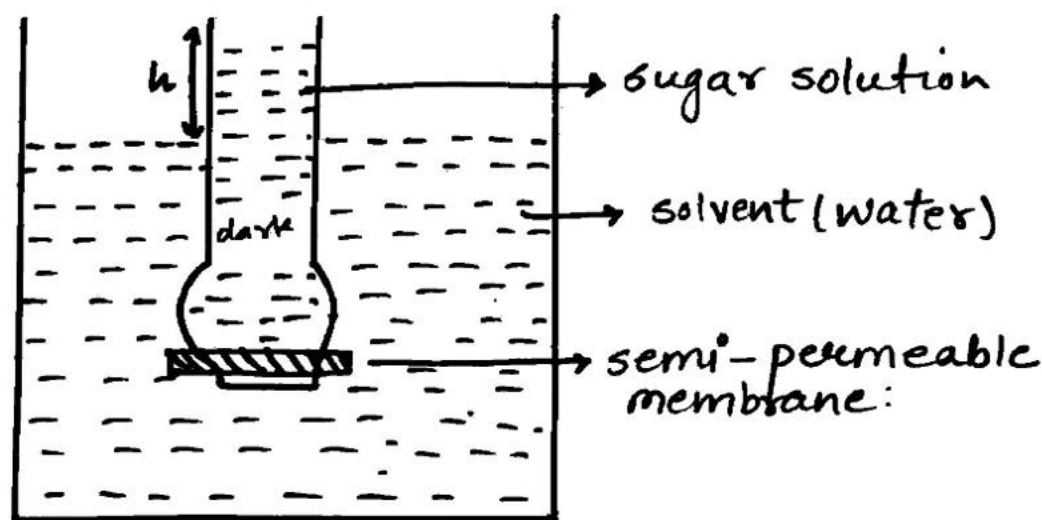


Fig:→ Osmosis

# Osmotic Pressure ( $\pi$ ) —• Concept:

When a solution and pure solvent are separated by a semi-permeable membrane, solvent molecules move into the solution (osmosis).

The pressure required to stop this flow is called osmotic pressure.

• Formula:

$$\pi = CRT$$

Where,

- $\pi$  = Osmotic pressure
- $C$  = Molar concentration of solute
- $R$  = Gas constant ( $0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ).
- $T$  = Temperature in Kelvin.

• Formula for molar mass:

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

where,  $V$  = volume of solution (in litres).

reverse osmosis.

- When a pressure greater than that of osmotic pressure is applied on solution side, then the solvent from the solution flows into pure solvent this process is called reverse osmosis.
- It used in desalination of sea water.

Isotonic Solutions

At a given temperature solutions of same osmotic pressure are called isotonic solutions:

eg: Blood is isotonic with saline (0.9% w/v NaCl solution).

If  $P_1 = P_2$  i.e., isotonic solutions

then  $\frac{n_1}{V_1} = \frac{n_2}{V_2}$  ;

$$\frac{W_1}{M_1 V_1} = \frac{W_2}{M_2 V_2}$$

**Hypotonic Solutions:** Solutions having lower osmotic pressure.

**Hypertonic Solutions:** Solutions having higher osmotic pressure.

### # Key points to Remember —

1. Colligative properties depend only on the number of solute particles, not their nature.
2. Used for determination of molar mass of solute.
3. If solute dissociates or associates, observed colligative properties deviate from the expected value.
4. Osmotic pressure is most reliable for molar mass of macromolecules.
5. Colligative properties are directly proportional to molality (except vapour pressure lowering).

# Questions for colligative properties: →

Q.1 At room temperature vapour pressure of pure water is 23.8 mm Hg. Mole fraction of sucrose in its aq. solution is 0.1 then vapour pressure of solution will be—

Ans—  $P^{\circ}$  (vapour pressure of pure water) = 23.8 mm Hg

Mole fraction of sucrose  $X_{\text{solute}} = 0.1$

$$X_{\text{water}} = 1 - 0.1 = 0.9$$

Vapour pressure of solution :

$$P = X_{\text{water}} \cdot P^{\circ} = 0.9 \times 23.8 = 21.42 \text{ mm Hg.}$$

Q.2 The molal freezing point constant of water is  $1.86 \text{ K molality}^{-1}$ . If 684 g of cane sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) is dissolved in 1000 g of water, the solution will freeze at —

Ans—  $K_f (\text{H}_2\text{O}) = 1.86 \text{ K kg mol}^{-1}$ .

mass of cane sugar = 684 g.

weight of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) =  $342 \text{ g mol}^{-1}$

$$\text{Moles Sucrose} = \frac{684}{342} = 2.0 \text{ mol.}$$

$$\text{molality (m)} = \frac{2.0 \text{ mol}}{1.0 \text{ kg}} = 2.0 \text{ m.}$$

$$\Delta T_f = K_f \times m = 1.86 \times 2 = 3.72^{\circ}\text{C}$$

Freezing point of pure water =  $0^{\circ}\text{C}$ , so

solution freezes at  $0 - 3.72 = -3.72^{\circ}\text{C}$ .

**Q.3.** An aqueous solution freezes at  $-0.186^{\circ}\text{C}$ . What is the elevation in boiling point? ( $K_f = 1.86$ ,  $K_b = 0.512$ )

**Ans-** solution freezes at  $-0.186^{\circ}\text{C}$ ,

$$\Delta T_f = 0 - (-0.186) = 0.186^{\circ}\text{C}$$

$$K_f = 1.86 \text{ (given)}$$

$$m = \frac{\Delta T_f}{K_f} = \frac{0.186}{1.86} = 0.1 \text{ m}$$

$$\therefore K_b = 0.512$$

$$\Delta T_b = K_b \times m = 0.512 \times 0.1 = 0.0512^{\circ}\text{C}$$

## # Abnormal Mass and Van't Hoff factor (i)

### • Introduction:

When we determine the molar mass of a solute using colligative properties (like boiling point elevation or freezing point depression), sometimes the calculated molar mass is different from the expected molar mass.

This happens because the solute either dissociates or associates in the solution.

This gives rise to abnormal molar masses.

### • Abnormal Molar Mass :→

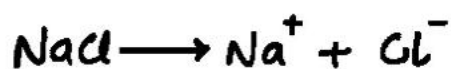
The molar mass obtained from colligative properties which differs from the expected molar mass is called abnormal molar mass.

### → Abnormal molar masses arise due to :

#### 1. Dissociation of solute —

- number of particles increases.
- colligative property increases
- observed molar mass decreases.

Example —



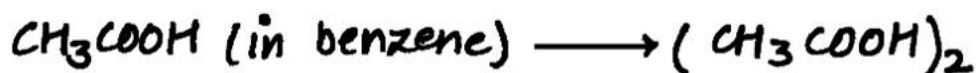
One molecule gives two ions → number of particle doubles.

Hence, observed molar mass becomes half the expected value.

#### 2. Association of solute —

- number of particles decreases,
- colligative property decreases
- observed molar mass increases.

Example —



Two molecules form one dimer → number of particles reduces by half.

Hence, observed molar mass becomes double the expected value.

# Van't Hoff Factor (i) :-

To correct these derivations, Van't Hoff introduced a factor 'i' which shows how many particles are actually present in solution compared to the number expected theoretically.

• Definition:

The Van't Hoff factor (i) is the ratio of the actual number of particles present in solution after association or dissociation to the number of formula units dissolved.

• Formula:

$$i = \frac{\text{observed colligative property}}{\text{calculated colligative property (assuming no dissociation/association)}}$$

or equivalently,

$$i = \frac{\text{Normal molar mass (theoretical)}}{\text{Observed molar mass}}$$

# Effect of (i) on colligative properties :-

All colligative property equations are modified by multiplying with i :-

| colligative property                   | original Formula                      | Corrected Formula              |
|----------------------------------------|---------------------------------------|--------------------------------|
| • Relative lowering of vapour pressure | $\frac{(P^\circ - P)}{P^\circ} = X_2$ | $(P^\circ - P)/P^\circ = iX_2$ |
| • Elevation in boiling point           | $\Delta T_b = K_b \times m$           | $\Delta T_b = iK_b \times m$   |

|                                |                             |                               |
|--------------------------------|-----------------------------|-------------------------------|
| • Depression in freezing point | $\Delta T_f = K_f \times m$ | $\Delta T_f = i K_f \times m$ |
| • Osmotic pressure             | $\pi = CRT$                 | $\pi = i CRT$                 |

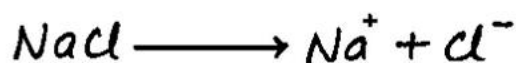
### • Van't Hoff Factor in Dissociation :→

Let's say one molecule splits into  $n$  ions and the fraction dissociated =  $\alpha$

Then,

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

**Example :**



Here ( $n=2$ )

If  $\alpha = 1$  (complete dissociation)

$$\text{then } i = 1 + (2-1) \times 1 = 2.$$

### • Van't Hoff Factor in Association :→

If some molecules associates, the factor becomes:

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

Where,

- $n$  = number of molecules forming 1 associated particle (e.g., dimer  $\longrightarrow n=2$ ).
- $\alpha$  = fraction of molecules associated

**Example:**

Acetic acid ( $\text{CH}_3\text{COOH}$ ) dimerizes in benzene  
 $n=2$

If  $\alpha=1$  (complete dimerization):

$$i = 1 - \frac{1(2-1)}{2} = 0.5$$

**# Uses of Van't Hoff Factor  $\rightarrow$** 

1. Corrects the equations of colligative properties.
2. Helps find degree of dissociation or association ( $\alpha$ ).
3. Helps calculate actual molar mass of solutes that dissociate or associate.

**# Questions  $\rightarrow$** 

1. Find  $i$  from molar masses,  
 Theoretical molar mass =  $84 \text{ g} \cdot \text{mol}^{-1}$   
 Observed molar mass =  $42 \text{ g} \cdot \text{mol}^{-1}$ . Find  $i$ ?

**Ans  $\rightarrow$**   $i = \frac{M_{\text{theo.}}}{M_{\text{obs.}}} = \frac{84}{42} = 2$

$i=2 \rightarrow$  the solute gives 2 particles per formula unit in solution (complete dissociation in 2 species)

2. Observed molar mass of  $\text{CaCl}_2 = 55.5 \text{ g} \cdot \text{mol}^{-1}$ .  
 Theoretical molar mass =  $111 \text{ g} \cdot \text{mol}^{-1}$ .  $\text{CaCl}_2$  dissociates as  $\text{CaCl}_2 \longrightarrow \text{Ca}^{2+} + 2\text{Cl}^-$  so  $n=3$ . Find degree of dissociation  $\alpha$ .

Ans →  $i = \frac{111}{55.5} = 2$

$$2 = 1 + 2\alpha \Rightarrow 2\alpha = 1 \Rightarrow \alpha = 0.5$$

$$\alpha = 0.50 \text{ (50 \% dissociation).}$$

3. Calculate the freezing point of a solution containing 60 g of glucose (Molar Mass =  $180 \text{ g mol}^{-1}$ ) in 250 g of water. ( $K_f$  of water =  $1.86 \text{ K kg/mol}^{-1}$ ).

Ans → We know  $\Delta T_f = K_f \times m$

$$m = \frac{60 / 180 \text{ mol}}{0.25 \text{ kg}} = 1.33 \text{ mol kg}^{-1}$$

$$\Delta T_f = 1.86 \times 1.33 \text{ K}$$

$$\Rightarrow \Delta T_f = 2.4738 \text{ K}$$

$$\Rightarrow T_f^\circ - T_f = 2.4738 \text{ K}$$

$$\Rightarrow T_f = T_f^\circ - 2.4738 \text{ K}$$

$$\Rightarrow = 273 - 2.4738 \text{ K} = 270.5262 \text{ K.}$$

**DREAMS  
DON'T WORK  
UNLESS  
YOU DO**





**Ans.(d)** Molar ratio of 1 : 1 means  $x_X = x_Y = 0.5$

$$P_{\text{total}} = x_X P_X^\circ + x_Y P_Y^\circ$$

$$\therefore 400 = 0.5 P_X^\circ + 0.5 P_Y^\circ$$

$$\text{or } P_X^\circ + P_Y^\circ = 800 \quad \dots(i)$$

Molar ratio of 1 : 2 means,  $x_X = \frac{1}{3}, x_Y = \frac{2}{3}$

$$\therefore 350 = \frac{1}{3} P_X^\circ + \frac{2}{3} P_Y^\circ$$

$$\text{or } P_X^\circ + 2 P_Y^\circ = 1050 \quad \dots(ii)$$

Eqn (ii) - Eqn. (i) gives  $P_Y^\circ = 250 \text{ mm}$

Putting in (i), we get  $P_X^\circ = 550 \text{ mm}$

- 6.** A solution containing 12.5 g of non-electrolyte substance in 185 g of water shows boiling point elevation of 0.80 K. Calculate the molar mass of a substance: ( $K_b = 0.52 \text{ K kg mol}^{-1}$ )

a.  $53.06 \text{ g mol}^{-1}$

b.  $25.3 \text{ g mol}^{-1}$

c.  $16.08 \text{ g mol}^{-1}$

d.  $43.92 \text{ g mol}^{-1}$

**Ans.(d)** 
$$M = \frac{K_b \times W_B}{\Delta T_b \times W_A} = \frac{0.52 \times 12.5}{0.80 \times 0.185}$$

$$= \frac{52 \times 125}{0.80 \times 185} = 43.92 \text{ g mol}^{-1}$$

(185 g = 0.185 Kg)

7. Osmotic pressure of a solution containing 2 g dissolved protein per 300 cm<sup>3</sup> of solution is 20 mm of Hg at 27°C. The molecular mass of protein is:
- a. 6239.3 g mol<sup>-1</sup>                      b. 12315.5 g mol<sup>-1</sup>  
 c. 3692.1 g mol<sup>-1</sup>                      d. 7368.4 g mol<sup>-1</sup>

Ans. (a)  $\pi = \frac{n_B RT}{V} : n_B = \frac{W_B}{M_B}$

$$\pi = \frac{W_B}{M_B} \times \frac{RT}{V} \Rightarrow M_B = \frac{W_B}{V} \times \frac{RT}{\pi}$$

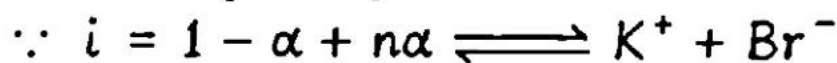
$$= \frac{2 \times 0.0821 \times 300 \times 760}{0.3 \times 20}$$

$$= 0.0821 \times 100 \times 760 = 6239.6 \text{ g mol}^{-1}$$

8. KBr is 80% dissociated in aqueous solution of 0.5 m concentration (given,  $K_f$  for water = 1.86 K Kg mol<sup>-1</sup>). The solution freezes at:
- a. 271.326 K    b. 272 K    c. 270.5 K    d. 268.5 K

Ans. (a)  $\Delta T_f = i \times K_f \times m$

Here; degree of dissociation = 80%



$$\therefore i = \frac{1 - 0.8 + 2 \times 0.8}{1} = 1.8$$

$$\therefore \Delta T_f = 1.8 \times 1.86 \times 0.5 \Rightarrow \Delta T_f = 1.674 \text{ K}$$

$$\Delta T_f = T_f^0 - T_f \Rightarrow 1.674 = 273 - T_f$$

$$T_f = 273 - 1.674 \Rightarrow T_f = 271.326 \text{ K}$$