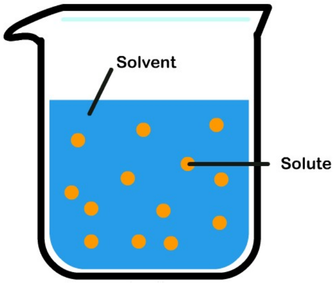
SOLUTIONS

- A solution is a homogeneous mixture of two or more pure substances whose composition can be varied within certain limits.

BINARY SOLUTION



- A solution consisting of two components is called a binary solution.
- The two components are as solute and solvent.
- The component present in excess is called the solvent.
- The component present in lesser quantity is called solute.

TYPES OF SOLUTIONS

- Classification is based on the physical state of the solute and solvent.

Types of solutions	Solute	Solvent	Examples
Solid Solutions	Solid	Solid	Copper dissolved in gold
	Liquid	Solid	Amalgam of Hg with Na
	Gas	Solid	Solution of H_2 in Palladium
Liquid Solutions	Solid	Liquid	Glucose dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Gas	Liquid	Oxygen dissolved in water
Gaseous Solutions	Solid	Gas	Camphor in Nitrogen gas
	Liquid	Gas	Chloroform mixed with Nitrogen gas
	Gas	Gas	Mixture of Oxygen and Nitrogen gas

METHODS FOR EXPRESSING CONCENTRATION OF SOLUTIONS

- Concentration is the amount of solute present per unit mass of solvent or solution.

1. MASS PERCENTAGE

- It is the mass of the component per 100g of the solution.
- $$\text{Mass percentage of solute} = \frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$$
- $$\text{Mass percentage of solvent} = \frac{\text{Mass of solvent}}{\text{Total mass of solution}} \times 100$$
- Eg: 10% glucose in water by mass means 10g of glucose is dissolved in 90g water resulting in a 100g solution.

QUESTION

What is the weight percentage of urea solution in which 10 gm of urea is dissolved in 90 gm water?

$$\text{Mass percentage of urea} = \frac{\text{Mass of urea}}{\text{Total mass of solution}} \times 100$$

$$\text{Mass percentage of urea} = \frac{10}{90 + 10} \times 100 = 10\%$$

2. VOLUME PERCENTAGE

- It is the volume of a component in mL present in 100 mL of the solution.
- $\text{Volume percentage of solute} = \dfrac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$
- $\text{Volume percentage of solvent} = \dfrac{\text{Volume of solvent}}{\text{Total volume of solution}} \times 100$
- Eg: 10% HCl solution in water means 10mL of HCl is dissolved in 90 mL water resulting in 100 mL solution.

3. MASS BY VOLUME PERCENTAGE

- It is the mass of the solute dissolved in 100 mL of the solution.
- $\text{Mass by volume percentage} = \dfrac{\text{Mass of solute}}{\text{Total volume of solution}} \times 100$
- Eg: A 10% mass by volume solution means that 10 gm solute is present in 100 mL of solution.

4. PARTS PER MILLION (ppm)

- Parts per million is used when a solute is present in trace quantities.
- It is the number of parts of a component per million parts of the solution.
- $\text{Parts per million} = \dfrac{\text{Mass of the component}}{\text{Mass of the solution}} \times 10^6$

5. MOLE FRACTION

- It is the ratio of number of moles of one component to the total number of moles present in the solution.
- $\text{Mole fraction of a component} = \dfrac{\text{No. of moles of the component}}{\text{Total No. of moles of all the components}}$
- Eg: In a binary mixture, if the number of moles of A and B is n_A and n_B respectively.

  Then, Mole fraction of A, $X_A = \dfrac{n_A}{n_A + n_B}$

  Mole fraction of B, $X_B = \dfrac{n_B}{n_A + n_B}$

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

$$X_A + X_B = 1$$

$$X_A = 1 - X_B$$

$$X_B = 1 - X_A$$

6. MOLARITY (M)

- It is the number of moles of solute dissolved in one litre of the solution.

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of the solution in litre}} \quad \textbf{or}$$

$$\text{Molarity (M)} = \frac{\text{Mass/Litre}}{\text{Molar Mass}} \quad \textbf{or} \quad \text{Molarity (M)} = \frac{W_B}{M_B} \times \frac{1000}{V}$$

- Thus, if one gram mole of a solute is present in 1 litre of the solution, the concentration of the solution is said to be one molar.
- Molarity is temperature dependent.

QUESTION

3.65 gm of HCl gas is present in 100 mL of its aqueous solution. What is the molarity?

$$\text{Molarity (M)} = \frac{W_B}{M_B} \times \frac{1000}{V\text{ (mL)}}, \quad \text{Molarity (M)} = \frac{3.65}{36.5} \times \frac{1000}{100} = 1\text{ M}$$

7. MOLALITY (m)

- It number of moles of the solute dissolved in one kilogram of the solvent.
- $\text{Molality (m)} = \frac{\text{No. of moles of the solute}}{\text{Mass of the solvent in kilogram}}$ **or** $\text{Molality (m)} = \frac{W_B}{M_B} \times \frac{1000}{W_A}$
- Thus, if 1 gram molecule of a solute is present in 1 kg of the solvent, the concentration of the solution is said to be one molal.
- Molality is the most convenient method to express the concentration because it involves the mass of liquids rather than their volumes.
- It is also independent of the variation in temperature.

8. NORMALITY (N)

- It is the number of gram equivalents of the solute dissolved in one litre of the solution.
- $\text{Normality (N)} = \frac{\text{No. of gram equivalents of solute}}{\text{Volume of the solution in litres}}$
- $\text{Normality (N)} = \frac{\text{Mass/Litre}}{\text{Equivalent Mass}}$ $\text{Normality (N)} = \frac{\text{Weight}}{\text{Equivalent Weight}} \times \frac{1000}{V\text{ (mL)}}$

NOTE

- Mass Percentage, Parts Per Million, mole fraction and molality are independent of temperature.
- Molarity is a function of temperature, because volume depends on temperature and the mass does not.

QUESTIONS

1. Calculate the molarity of a solution containing 5g of NaOH in 450 ml of solution

$$\text{Molarity (M)} = \frac{W_B}{M_B} \times \frac{1000}{V}, \quad \text{Molarity (M)} = \frac{5}{40} \times \frac{1000}{450} = 0.278\text{moles/Litre}$$

2. Calculate the molality of 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene

$$\text{Molality (m)} = \frac{W_B}{M_B} \times \frac{1000}{W_A}, \quad \text{Molarity (M)} = \frac{2.5}{60} \times \frac{1000}{75} = 0.556 \text{ moles/kg}$$

3. Find the mole fraction of ethylene glycol in a solution containing 20% of $C_2H_6O_2$ by mass?
20% ethylene glycol means 20g of ethylene glycol in 100g of solution.

Mass of glycol = 20g
Mass of water = 100- 20 = 80g

$$\text{No. of moles of glycol (N)} = \frac{\text{Mass}}{\text{Molar Mass}} \quad \text{No. of moles of glycol (N)} = \frac{20}{62} = 0.322 \text{ mol}$$

$$\text{No. of moles of water (N)} = \frac{\text{Mass}}{\text{Molar Mass}} \quad \text{No. of moles of water (N)} = \frac{80}{18} = 4.44 \text{ mol}$$

$$\text{Mole fraction of ethylene glycol} = \frac{n_{glycol}}{n_{glycol} + n_{water}} = \frac{0.322}{0.322 + 4.44} = 0.0676$$

SOLUBILITY

- It is its maximum amount of substance that can be dissolved in a specified amount of solvent at a specified temperature.

SOLUBILITY OF A SOLID IN A LIQUID

- Solubility of Solid Solute in Liquid Solvent: depends on nature of solute and solvent.
- Ionic/polar compounds like NaCl, KCl etc dissolves in polar solvent like water.
- The non-polar/covalent or organic molecules can dissolve in non-polar compounds like benzene.
- When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This ability of the solute to dissolve in a solvent 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.**
- A stage is reached when the two processes occur at the same rate. Under such conditions, number of solute particles going into solution will be equal to the solute particles separating out and a state of **dynamic equilibrium** is reached.

$$\text{Solute} + \text{Solvent} \rightleftarrows \text{Solution}$$

- A solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution.**
- A solution in which more solute can be dissolved at the same temperature is called an **unsaturated solution.**

FACTORS AFFECTING SOLUBILITY

1. NATURE OF SOLUTE AND SOLVENT

- Strong solute-solvent attractions increase the solubility while weak solute-solvent attractions decrease the solubility.

- Polar solutes tend to dissolve best in polar solvents while non-polar solutes tend to dissolve best in non-polar solvents.

2. TEMPERATURE

- In a nearly saturated solution, the dissolution process is endothermic ($\Delta_{sol} H > 0$), the solubility should increase with rise in temperature.
- If the process is exothermic, ($\Delta_{sol} H < 0$) the solubility should decrease.
- Solubility of gases in liquids decreases with rise in temperature.
- When dissolved, the gas molecules are present in liquid phase and the process of dissolution is an exothermic process.
- Therefore, the solubility should decrease with increase of temperature.

3. PRESSURE

- Pressure does not have any significant effect on solubility of solids in liquids.
- Because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

Qn. Aquatic life is more comfortable in cold water than warm water. Why?

- When temperature is low, solubility will be high.
- So cold water contains more dissolved oxygen than warm water.
- Therefore, aquatic life is more comfortable in cold water.

SOLUBILITY OF A GAS IN A LIQUID

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 law states that, the mole fraction of a gas in the solution is proportional to the partial pressure of the gas over the solution.

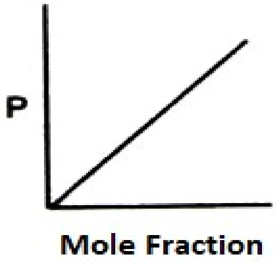
OR

- The partial pressure of the gas in vapour phase (P) is proportional to the mole fraction of the gas (x) in the solution. $P = K_H.x$

  Where K_H is Henry's law constant.

GRAPHICAL REPRESENTATION OF HENRY'S LAW

- Pressure α Mole fraction
- $P \ \alpha \ X$
- $P = K_H X$
- K_H = Henry's Law Constant
- Slope of the graph = Henry's Law Constant



CHARACTERISTICS OF K_H

1. Different gases have different K_H values at the same temperature. This suggests that K_H

is a function of the nature of the gas.

Nitrogen at 293K $K_H = 76$

Oxygen at 293 K $K_H = 34$

2. Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid. $P = K_H X$
3. The solubility of gases increases with decrease of temperature.

Nitrogen at 293 K $K_H = 76$

Nitrogen at 303 K $K_H = 88$

Nitrogen at 293 K $K_H = 34$

Nitrogen at 303 K $K_H = 46$

APPLICATIONS OF HENRY'S LAW

1. In packing of soda cans

- All carbonated drinks are bottled under high pressure to increase the solubility of CO_2 in solution.
- When the bottle is opened, the pressure above the solution decreases and some of carbon dioxide bubbles are released off, which leads to effervescence / fizz.

2. In Deep see diving

- When Scuba divers come towards the surface of water, the pressure gradually decreases.
- This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood.
- This blocks the capillaries and creates a medical condition known as **bends**.
- To avoid bends, the tanks used by Scuba Divers is filled with air and diluted with Helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

3. For Climbers or People living in high altitudes

- For Climbers or people living at high altitudes, the concentration of oxygen in blood and tissues are low.
- Due to this, climbers become weak and unable to think clearly.
- This leads to a condition known as **Anoxia**.

4. The fishes and other aquatic life survive inside the water bodies in polar areas where water is freezed on the top.
5. Thermal power plants that discharges the hot water into water bodies like ponds, rivers or lakes may kill the fish by decreasing the dissolved oxygen concentration in it.

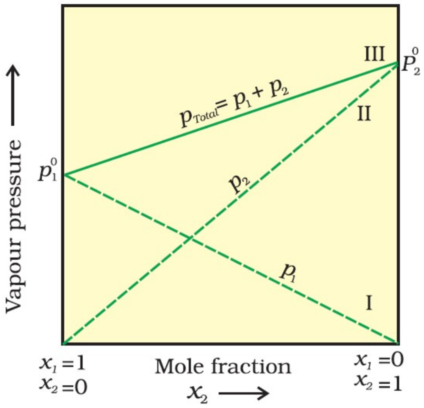
VAPOUR PRESSURE OF LIQUID SOLUTIONS

- It is the pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature.

VAPOUR PRESSURE OF LIQUID-LIQUID SOLUTIONS

Raoult's Law

- Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.
- Consider a binary solution of two volatile liquids A and B.
- If P_A and P_B are the partial vapour pressures of the two liquids and X_A and X_B are their mole fractions in solution.
- Then, $P_A = P_A^0.X_A$, $P_B = P_B^0.X_B$
- Where P_A^0 and P_B^0 are the vapour pressures of the pure components A and B respectively.



RAOULT'S LAW IN COMBINATION WITH DALTON'S LAW OF PARTIAL PRESSURE

- Assuming that vapours of a liquid is behaving like an ideal gas, then according to Dalton's law of partial pressure, the total pressure P_T is given by
- $P_T = P_A + P_B$
- $P_T = P^0{}_A.X_A + P^0{}_B.X_B$
- We know that $X_A + X_B = 1$, Then $X_A = 1 - X_B$
- $P_T = P^0{}_A.(1 - X_B) + P^0{}_B.X_B$
- $P_T = P^0{}_A - P^0{}_A.X_B + P^0{}_B.X_B$
- $P_T = P^0{}_A + (P^0{}_B - P^0{}_A)\,X_B$

RAOULT'S LAW AS A SPECIAL CASE OF HENRY'S LAW

- Only the proportionality constant K_H differs from P_A^0.
- According to Raoult's Law $P_A = P_A{}^0.X_A$
- According to Henry's Law $P = K_H.X$
- Only the proportionality constant K_H differs from P_A^0.
- Therefore, Raoult's law become a special case of Henry's law when $K_H = P_A{}^0$

IDEAL AND NON IDEAL SOLUTIONS

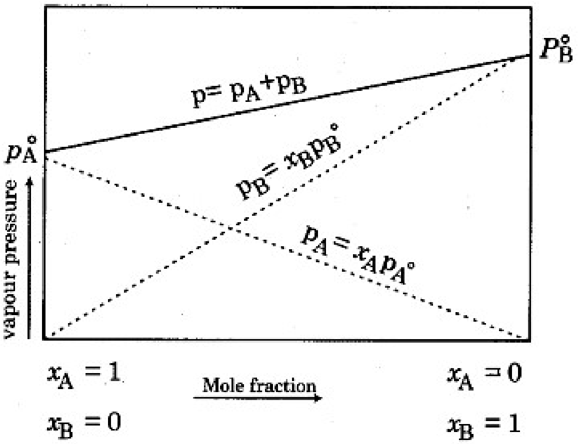
- The binary solutions may be of two types.

1. IDEAL SOLUTIONS

- Ideal solutions are those which obey Raoult's law exactly at all concentrations and at all temperatures.

- Let P_A and P_B are the partial vapour pressures and X_A and X_B are the mole fractions of these volatile components A and B respectively.
- Then according to Raoult's law we can write,
- $P_A = P_A^0.X_A$, $P_B = P_B^0.X_B$
- According to Dalton's law of partial pressures, the total vapour pressure is given by
- $P = P_A + P_B$, $P = P_A^0.X_A + P_B^0.X_B$

GRAPHICAL REPRESENTATION FOR AN IDEAL SOLUTION



- An ideal solution is one which obeys Raoult's law at all concentrations and temperatures.
- The essential characteristics of ideal solutions are

1) Obeys Raoult's law at all concentrations and temperatures.
2) $\Delta H_{mix} = 0$
3) $\Delta V_{mix} = 0$

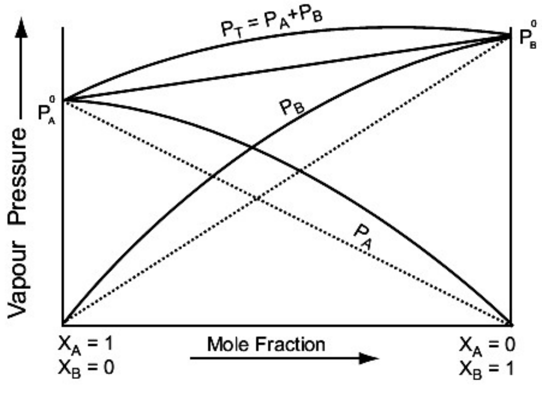
2. NON IDEAL SOLUTIONS

- Solutions which do not obey Raoult's law at all concentrations and temperatures are called non ideal solutions.
- For a non-ideal solution containing the volatile components A and B,
- $P_A \neq P_A^0.X_A$, $P_B \neq P_B^0.X_B$
- The essential characteristics of non-ideal solutions are
- Does not obey Raoult's law at all concentrations and temperatures.
- $\Delta H_{mix} \neq 0$,
- $\Delta V_{mix} \neq 0$

TYPES OF NON IDEAL SOLUTIONS

- Non ideal solution show +ve and —ve deviation from Raoult's law depending upon their nature.

1. POSITIVE DEVIATIONS FROM RAOULTS LAW



- In this type, the vapour pressure of each component of the solution is greater than the vapour pressure as expected by Raoult's law.
- The total vapour pressure of the solution is higher than that of an ideal solution of the same

composition.

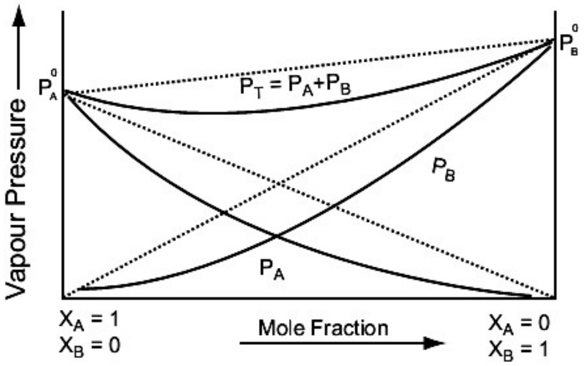
- In these solutions, ΔH_{mixing} and ΔV_{mixing} are +ve.

CAUSE OF POSITIVE DEVIATION

- In this type, the attractive forces between solvent and solute molecules are weaker than those between solute molecules or between solvent molecules and leads to increase in vapour pressure resulting in positive deviations.
- Eg: Acetone and Carbon disulphide, Benzene and acetone, Ether and Acetone.

NEGATIVE DEVIATIONS FROM RAOULTS LAW

- In this, both the components have partial pressures, less than that expected from Raoult's law.
- As a result, the total vapour pressure of the solution is lower than that of an ideal solution of the same composition. Here both ΔH_{mixing} and ΔV_{mixing} are —ve.



CAUSE OF NEGATIVE DEVIATION

- In this type of deviations, the solute-solvent interactions are stronger than the solvent—solvent or solute—solute interactions and lead to decrease in vapour pressure resulting in —ve deviations.
- Eg: Benzene and Chloroform, Chloroform and Nitric acid, Chloroform and ether etc.

QUESTION

Why is the Vapour pressure of a liquid decreases when non - volatile solute is added to it OR vapour pressure of solution is less than that of pure solvent?

- When a non-volatile solute is added to pure solvent some of the solvent molecule at the surface is replaced by solute molecule.
- Therefore, Vapour pressure decreases.

AZEOTROPES

- The solutions which boil at a constant temperature and distill over completely at the same temperature without any change in composition are called constant boiling mixtures or azeotropes.

1. MINIMUM BOILING AZEOTROPES

- The solutions that show large positive deviations from Raoults law is called Minimum Boiling Azeotropes.
- Eg: 95.6% ethanol and 4.4% H_2O by volume.

2. MAXIMUM BOILING AZEOTROPES

- The solutions that show large negative deviations from Raoults law is called Maximum

Boiling Azeotropes.

- Eg: 21.2% HCl and 78.8% H_2O by weight, 68% HNO_3 and 32% H_2O by weight.

COLLIGATIVE PROPERTIES

- The properties of a solution which depend only on the number of solute particles but not on the nature of the solute are called colligative properties.
- **The important colligative properties are**
- Relative Lowering of Vapour Pressure
- Elevation of Boiling Point
- Depression of Freezing Point
- Osmotic Pressure

1. RELATIVE LOWERING OF VAPOUR PRESSURE

- Vapour pressure is the escaping tendency of the liquid from the surface of solution.
- In **solution**, a part of the liquid surface is occupied by non-volatile solute particles.
- Therefore, evaporation of the liquid will take place from a lesser surface area.
- This is referred to as the Lowering of Vapour Pressure.
- According to Raoult's law, the relative lowering of vapour pressure of a solution is equal to the mole fraction of the non-volatile solute.

$$P_A = P_A^0 . X_A$$

$$X_A = 1 - X_B$$

$$P_A = P_A^0 (1 - X_B)$$

$$\frac{P_A}{P_A^0} = 1 - X_B$$

$$1 - \frac{P_A}{P_A^0} = X_B$$

$$\frac{P_A^0 - P_A}{P_A^0} = X_B$$

$$P_A^0 - P_A = P_A^0 . X_B, \quad \text{i.e., } P_A^0 - P_A \;\alpha\; X_B$$

- Thus the lowering of vapour pressure $(P_A^0 - P_A)$ depends only on the mole fraction of the solute. So it is a colligative property.

DETERMINATION OF MOLAR MASS

- According to Raoult's law, the relative lowering of vapour pressure is equal to the mole fraction of the solute.

$$\frac{P_A^0 - P_A}{P_A^0} = X_B$$

$$\text{But } X_B = \frac{n_B}{n_A + n_B}, \quad n_A = \frac{W_A}{M_A} \quad \text{and} \quad n_B = \frac{W_B}{M_B}$$

- For a dilute solution, $n_B << n_A$

$$X_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A}$$

W_A = Weight of solvent

$$X_B = \frac{W_B.M_A}{M_B.W_A}$$

W_B = Weight of solute

$$\text{i.e., } \frac{P_A^0 - P_A}{P_A^0} = \frac{W_B.M_A}{M_B.W_A}$$

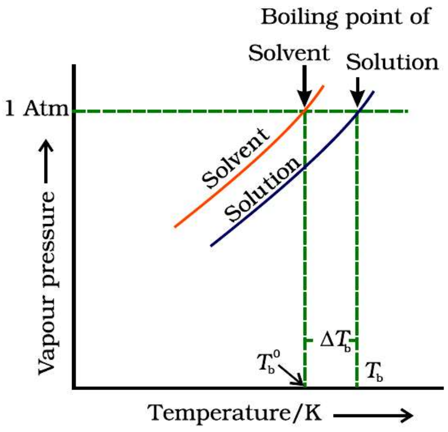
M_A = Molecular mass of solvent

$$M_B = \frac{P_A^0.W_B.M_A}{(P_A^0 - P_A).W_A}$$

M_B = Molecular mass of solute

2. ELEVATION OF BOILING POINT

- The boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.
- The boiling point of a solution (T_b) containing a non volatile solute is always greater than that of the pure solvent (T_b^0).
- The effect of adding a non volatile solute on the boiling point and vapour pressure is represented graphically.
- In the graph, at T_b^0 the vapour pressure of the solution is less than the vapour pressure of the pure solvent.
- Therefore the solution does not boil at T_b^0.
- But it boils at an elevated temperature T_b.
- Where the vapour pressure of the solution becomes equal to the atmospheric pressure.
- The difference between the boiling points of the solution (T_b) and the solvent (T_b^0) is called elevation of boiling point (ΔT_b).



$$\Delta T_b = T_b - T_b^0$$

- It is found that the elevation of boiling point is directly proportional to the number of moles the solute in a given amount of solvent.

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b.m$$ Where K_b is called Ebullioscopic Constant

- When m = 1, $\Delta T_b = K_b$
- The **molal elevation constant or Ebullioscoppic constant (K_b)** is defined as the elevation of boiling point produced by the dissolution of 1 mole of a non volatile solute in 1000g of the solvent.

DETERMINATION OF MOLAR MASS

- A known mass of the solute is dissolved in a known mass of solvent.
- Noting the boiling point of solvent and that of solution, the elevation of boiling point is determined.
- From these values, the molar mass of the solute can be calculated.

$$\Delta T_b = K_b.\text{molality}$$

$$\text{Molality (m)} = \frac{\text{No. of moles of the solute}}{\text{Mass of the solvent in gram}} \times 1000$$

- No. of moles of the solute = $\frac{W_B}{M_B}$

$$m = \frac{W_B.1000}{M_B.W_A}$$

$$\Delta T_b = \frac{K_b.W_B.1000}{M_B.W_A}, \quad M_B = \frac{K_b.W_B.1000}{\Delta T_b.W_A}$$

APPLICATIONS

- Sea water freeze at low temperature than distilled water but boils at higher temperature.
- Sea water contain dissolved salts. Therefore, boiling point increases & freezing point decreases.
- To get hard boiled eggs, sodium chloride is added to water. Addition of salt or other non-volatile solid reduces the vapour pressure of the liquid and consequently the boiling point increases and the water can attain a temperature higher than 100^{0}C before starting to boil. This helps cook and hard boil the egg quicker. Addition of salt to water before or while heating will increase its boiling point.
- The addition of coolant helps to raise the **boiling point** of the water to prevent the radiator from overheating.
- Refining of sugar from sugar cane solution.

QUESTIONS

1. On dissolving 10.8 glucose (molar mass = 180) in 240g of water, its boiling point increases by 0.13°C. Calculate the molal elevation constant of water.

Given, ΔT_b =0.13°C, W_A = 240 g, M_B = 180 and W_B = 10.8 g

$$\Delta T_b = \frac{K_b.W_B.1000}{M_B.W_A}, \quad K_b = \frac{\Delta T_b.W_A.M_B}{1000.W_B} \quad K_b = \frac{0.13 \times 240 \times 180}{1000 \times 10.8} = 0.52\ ^{\circ}C$$

2. A solution of 2.5g of a non-volatile solute in 100g benzene, boiled at 0.42°C higher than the boiling point of pure benzene. Calculate the molecular mass of the substance. Molal elevation constant of benzene is 2.67 K kg mol^{-1}.

Given, $K_b = 2.67$, $W_B = 2.5$ g, $W_A = 100$ g, $\Delta T_b = 0.42$

$$M_B = \frac{K_b.W_B.1000}{\Delta T_b.W_A}, \quad M_B = \frac{2.67 \times 2.5 \times 1000}{0.42 \times 100} = 158.9$$

3. The molal elevation constant for water is 0.56 K kg mol^{-1}. Calculate the boiling point of a solution made by dissolving 6.0 g of urea (NH_2CONH_2) in 200 g of water.

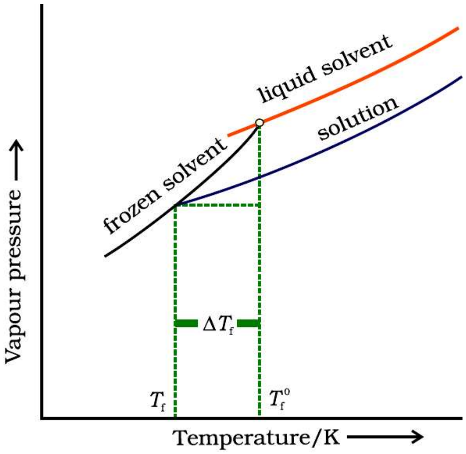
Given, $K_b = 0.56$ K kg mol^{-1}, $W_B = 6.0$ g, $W_A = 200$ g, $M_B=60$

$$\Delta T_b = \frac{K_b.W_B.1000}{M_B.W_A}, \quad \Delta T_b = \frac{0.56 \times 6 \times 1000}{60 \times 200} = 0.28^{\circ}C$$

Thus, The boiling point of solution = B.P. of water + ΔT_b = (100°C + 0.28°C) = 100.28°C

3. DEPRESSION OF FREEZING POINT

- The freezing point of a liquid is defined as the temperature at which the liquid and solid states of the substance have the same vapour pressure.
- The freezing point of a solution (T_f) containing a non volatile solute is always less than that of the pure solvent (T_f^0).
- The effect of adding a non volatile solute on the freezing point and vapour pressure is represented graphically.
- In the graph at T_f^0, the vapour pressure of the solution is less than the vapour pressure of the pure solvent.



- Therefore, the solution does not freeze at T_f^0.
- It freeze at a depressed temperature (T_f), where the vapour pressure of the solution becomes equal to the atmospheric pressure.
- The difference in freezing point between the pure solvent T_f^0 and that of the solution (T_f), is called depression in freezing point, ΔT_f.

$$\Delta T_f = T_f^0 - T_f$$

- For a dilute solution, the mole fraction of the solute is directly proportional to the molality of the solution.

$$\text{i.e.,} \quad \Delta T_f \; \alpha \; \text{molality}$$

$$\Delta T_f = K_f.\text{molality}$$

- Where K_f is called Cryoscopic Constant.

When m = 1, $\Delta T_f = K_f$

- **Molal Depression Constant or Cryoscopic constant (K_f)** is defined as the depression of freezing point produced by the dissolution of 1 mole of a solute in 1000g of the solvent.
- Since ΔT_f is proportional to molality, ΔT_f is a colligative property.

DETERMINATION OF MOLAR MASS

- A known mass of the solute is dissolved in a known mass of the solvent and the freezing point depression ΔT_f is determined.

$$\Delta T_f = K_f.\text{molality}$$

- $\text{Molality (m)} = \dfrac{\text{No. of moles of the solute}}{\text{Mass of the solvent in gram}} \times 1000$
- $\text{No. of moles of the solute} = \dfrac{W_B}{M_B}$

$$m = \frac{W_B.1000}{M_B.W_A}$$

$$\Delta T_f = \frac{K_f.W_B.1000}{M_B.W_A}, \qquad M_B = \frac{K_f.W_B.1000}{\Delta T_f.W_A}$$

APPLICATIONS

- In cold climate, ethylene glycol is added to water in the car radiator as antifreeze.
- During winter, salt is sprinkled on the road to lower the freezing point.
- Sea water freeze at low temperature than distilled water.
- Sea water contain dissolved salts. Therefore, boiling point increases & freezing point decreases

QUESTIONS

1. On dissolving 0.25g of a non-volatile substance in 30mL benzene (density 0.8 g/mL), its freezing point decreases by 0.40°C. Calculate the molecular mass of non-volatile substance (K_f = 5.12 K kg mol^{-1}).

Given, K_f = 5.12 K kg mol^{-1}, W_B = 0.25 g, ΔT_f = 0.40°C.

Mass of benzene, W_A = volume × density = 30 × 0.8 = 24 g

$$M_B = \frac{K_f.W_B.1000}{\Delta T_f.W_A}, \quad M_B = \frac{5.12 \times 0.25 \times 1000}{0.40 \times 24} = 133.33$$

2. By dissolving 13.6g of a substance in 20g of water, the freezing point decreased by 3.7°C. Calculate the molecular mass of the substance. [Molal depression constant for water = 1.863 K kg mol^{-1}]

Given, K_f = 1.863 K kg mol^{-1}, W_B = 13.6 g, W_A = 20 g, ΔT_f = 3.7°C

$$M_B = \frac{K_f . W_B . 1000}{\Delta T_f . W_A}, \quad M_B = \frac{1.863 \times 13.6 \times 1000}{20 \times 3.7} = 243.39$$

4. OSMOSIS & OSMOTIC PRESSURE

OSMOSIS

- The phenomenon of spontaneous flow of a solvent through a semi permeable Membrane (SPM), from the pure solvent to the solution.
- Or from a dilute solution to a concentrated solution is called osmosis.

OSMOTIC PRESSURE

- The excess pressure which must be applied to the solution to prevent the flow of solvent from its side to solution side across a semi permeable membrane is called osmotic pressure.

SEMIPERMEABLE MEMBRANE

- A membrane which allows only the flow of solvent molecules and not the solute molecules is called semi permeable membrane.

LAW'S OF OSMOTIC PRESSURE

1. VANT HOFF BOYLE'S LAW

- The law states that, the osmotic pressure of a solution is directly proportional to the molar concentration at a given temperature.

i.e., $\pi \alpha c$

- Where 'π' is the osmotic pressure and 'c' is the concentration.

2. VANT HOFF CHARLE'S LAW

- The law states that the osmotic pressure of a solution at a given concentration is proportional to the absolute temperature 'T'.
- i.e., $\pi \alpha T$
- On combining the above two laws

$$\pi \alpha CT$$

$$\pi = CRT, \qquad \text{But } C = \frac{n}{V}$$

- Therefore, $\pi = \frac{nRT}{V}$

$$\pi V = nRT$$

DETERMINATION OF MOLAR MASS

- According to Van't Hoff Equation

$$\pi V = nRT$$

$$n = \frac{W_B}{M_B}$$

- Where W_B and M_B are the mass and molar mass of solute.

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

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

NOTE

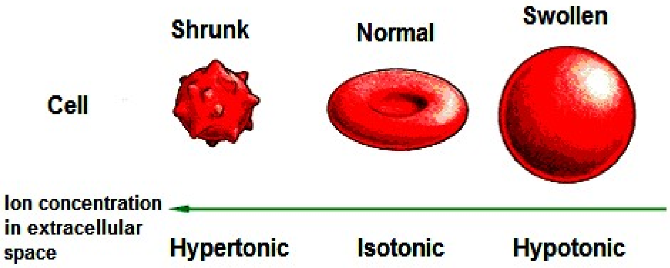
DETERMINATION OF MOLECULAR MASS OF POLYMERS

- For determining the molecular mass of polymers, osmotic pressure is preferred due to the following reasons.
- Poor solubility of the polymers.
- Polymers are not stable at higher temperatures.
- Osmotic pressure measurements can be done at room temperature.
- Molecular Mass can be measured more accurately.
- Molarity is used instead of molality.

ISOTONIC SOLUTIONS, HYPERTONIC SOLUTIONS & HYPOTONIC SOLUTIONS

- de-Vries developed an approximate method for comparing the relative osmotic pressures of aqueous solutions

- Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.
- A solution of greater osmotic pressure when compared to other solution is called a hypertonic solution.
- A solution whose osmotic pressure is less than the other solution is called hypotonic solution.



EXAMPLES OF OSMOSIS

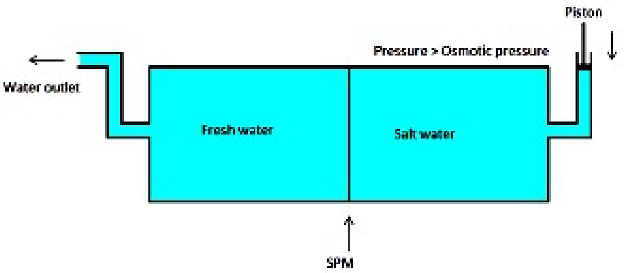
- If we place blood cells in the solution containing more than 0.9% Nacl, water will flow out of the cells and they would shrink. (Hypertonic)
- If we place blood cells in the solution containing less than 0.9% NaCl, water will flow into the cells and they would swell. (Hypotonic)
- A raw mango placed in concentrated salt solution loses water via osmosis and shrivel into pickle.
- Wilted flowers revive when placed in fresh water.
- A carrot that has become limp because of water loss into the atmosphere can be placed

into the water making it firm once again.

- People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis.
- Edema – Retention of water in intercellular spaces of people taking salty food due to osmosis.
- When a plant cell is placed in hypotonic solution, the water is drawn in and the cell swells.
- If the cell is placed in a hypertonic solution, water will diffuse out of the cell fluid and partial collapse of the cell will take place. (plasmolysis)

REVERSE OSMOSIS

- The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side.
- i.e., the pure solvent flows out of the solution through semi permeable membrane. This phenomenon is called reverse osmosis.
- Reverse Osmosis finds application in Desalination of sea water & Purification of water.



APPLICATIONS OF OSMOSIS

- Capillary rise of liquids.
- Absorption of water from soil into plants.
- Preservation of meat by salting (adding NaCl)
- Preservation of fruits by adding sugar (Candid fruit, Cherry)

QUESTION

1. RBC placed in NaCl solution having concentration greater than 0 .91% will shrink. Why?

Ans. Osmosis (flow of solvent) from RBC to NaCl

2. Arginine vasopressin is a pituitary hormone. It helps to regulate the amount of water in the body by reducing the flow of urine form kidneys. An aqueous solution containing 21.6 mg of vasopressin in 100 mL of solution had an osmotic pressure of 3.70 mm Hg at 25°C. What is molecular weight of hormone?

Given $W_B = (21.6\times 10^{-3}\text{ g})$, $M_B = ?$ $R = 0.0821\text{ L atm K}^{-1}\text{ mol}^{-1}$,

$T = 298\text{ K}$, $V = 100/1000 = 0.1\text{ L}$: $\pi = 3.70/760\text{ atm} = 0.00486$

$$M_B = \frac{W_B RT}{\pi V} \qquad M_B = \frac{21.6 \times 10^{-3} \times 0.0821 \times 298}{0.00486 \times 0.1} = 1085\text{ g/mol}$$

3. A solution is prepared by dissolving 1.08g of human serum albumin in 50cm^3 of aqueous solution. The solution has an osmotic pressure of 5.85mm Hg at 298K. What is molar mass of albumin?

Given $W_B = 1.08$ $R = 0.0821$ litre atm K^{-1} mol^{-1} $T = 298$ K,

$\pi = 5.85/760$ atm = 0.00769 $V = 50/1000 = 0.05$ litre

$$M_B = \frac{W_B RT}{\pi V} \qquad M_B = \frac{1.08 \times 0.0821 \times 298}{0.00769 \times 0.05} = 68655 \text{ g/mol}$$

4. Calculate osmotic pressure of 5% solution of cane sugar ($C_{12}H_{22}O_{11}$) at 15°C.

$M_B = 342$, $W_B = 5$ g $V = 100$ mL = 0.1 litre

$R = 0.082$ $T = (15 + 273) = 288$ K

$$\pi V = \frac{W_B RT}{M_B}, \quad \pi = \frac{W_B RT}{V.M_B}, \quad \pi = \frac{5 \times 0.082 \times 288}{0.1 \times 342} = 3.453 \text{ atm}$$

5. The solution containing 10g of an organic compound per litre showed an osmotic pressure of 1.16 atm at 0°C. Calculate the molecular mass of the compound. Given R = 0.0821 litre atm per degree per mol.

Given $W_B = 10g$ $\pi = 1.16$ atm $V = 1$ litre $R = 0.0821$ and $T = 273$ K.

$$M_B = \frac{W_B RT}{\pi V} \qquad M_B = \frac{10 \times 0.0821 \times 273}{1.16 \times 1} = 189.94$$

ABNORMAL MOLAR MASS

- The wrong values of molar masses obtained from colligative properties due to association or dissociation of molecules in solution is called abnormal molar mass.

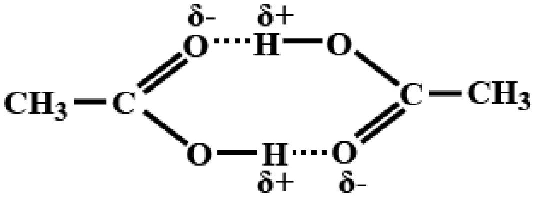
1. ABNORMAL MOLAR MASS DUE TO ASSOCIATION

- Association is a process in which two or more molecules combine to form a bigger molecule.
- Due to association, there will be decrease in the number of particles.
- As a result, there is a decrease in the value of colligative properties.
- Hence the observed values of molar mass will be greater than the normal values.

EXAMPLES

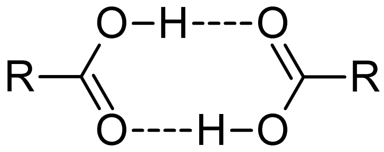
A) Dimerisation of Acetic Acid in Benzene

- Molecules of Ethanoic Acid (Acetic Acid) dimerise in benzene due to hydrogen bonding.
- Dimerisation occurs in solvent with low dielectric constant.
- The number of particles is reduced due to dimerization.
- Hence the observed values of molar mass will be greater than the normal values.



B) Dimerisation of Benzoic Acid in Benzene

- Molecules of Benzoic Acid (C_6H_5COOH) dimerise in benzene due to hydrogen bonding.
- Dimerisation occurs in solvent with low dielectric constant.
- The number of particles is reduced due to dimerization.
- Hence the observed values of molar mass will be greater than the normal values.



2. ABNORMAL MOLAR MASS DUE TO DISSOCIATION

- If dissociation occurs, the number of solute particles increases.
- It results in an increase in the values of colligative properties.
- Hence the observed values of molar mass will be lower than the normal values.

  Eg. $NaCl$, KCl, $BaCl_2$, $AlCl_3$ ………………….

1) $NaCl \longrightarrow Na^+ + Cl^-$

- No. of particles doubled
- Colligative property doubled
- Mol. Mass reduced to half (M/2)

2) $BaCl_2 \longrightarrow Ba^{2+} + 2Cl^-$

- No. of particles tripled
- Colligative property tripled
- Molar mass is reduced to M/3

VANT HOFF FACTOR

- To account for the abnormal molar mass, Van't Hoff introduced a factor 'i' known as Van't Hoff factor.
- It is the ratio of the observed colligative property to the theoretical colligative property.

OR

- It is the ratio of normal molar mass to the observed molar mass.

$$i = \frac{\text{Observed Colligative Property}}{\text{Theoretical Colligative Property}}$$

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

$$i = \frac{\text{No. of particles after dissociation / association}}{\text{No. of particles before dissociation / association}}$$

MODIFIED EQUATIONS FOR COLLIGATIVE PROPERTIES

- If Vant Hoff Factor " i " is included, the equations for colligative properties can be modified as follows.
- $\frac{P_A^0 - P_A}{P_A^0} = i X_B$ (X_B-mole fraction of the solute)
- $\Delta T_b = i K_b m$
- $\Delta T_f = i K_f m$
- $\pi = i CRT$

Values of Vant Hoff Factor 'i' for Various Solutes and their Corresponding Molecular Mass

Solute	Solvent	Van't Hoff Factor (i)	Theoretical Molecular Mass	Experimental Molecular Mass
NaCl Dissociation	Water	2, $i > 1$	A	A/2
$AlCl_3$ Dissociation	Water	4, $i > 1$	B	B/4
$BaCl_2$ Dissociation	Water	3, $i > 1$	C	C/3
CH_3COOH Association	Benzene	½, $i < 1$	D	2D
Urea-Nonelectrolyte-No change	Water	1, $i = 1$	E	E
Benzoic acid Association	Benzene	½, $i < 1$	F	2F