

Solutions and Colligative Properties

Introduction:

Solutions: Mixture of two or more components.

Depending on size of components, mixtures are classified into 3 types.

a) **Coarse mixture:**

Definition: The mixture which contains components having relatively bigger size is called as coarse mixture. E.g. Mixture of salt and sugar.

b) **Colloidal dispersion:**

Definition: The mixture which is formed when the size of particles dispersed in solvent are in the range of 10^{-7} cm to 10^{-4} cm is called as colloidal dispersion.

Properties of colloidal particles/solutions.

- 1) Colloidal particles carry positive or negative charge which stabilizes colloidal dispersion. E.g. Ferric hydroxide sol, arsenic sulphide sol.
- 2) Colloidal solutions are heterogeneous and can be easily separated.

c) **True solution:**

Definition: It is defined as the homogeneous mixture of two or more substances, the composition of which is not fixed and may be varied within certain limits.

Properties of true solution:

- 1) Size of particles dissolved in the solvent are very small of the order of 10^{-8} cm
- 2) It is homogenous.
- 3) It cannot be separated into components by simple mechanical method.

Composition of solution -

- a) **Solute:** The component which constitutes smaller part of solution is called as solute.
- b) **Solvent:** The component which constitutes larger part of solution is called as solvent.

Homogeneous solution:

Definition- The solution whose composition is uniform throughout the body of the solution is called as homogeneous solution.

Formation/Preparation: The homogeneous solution is formed due to force of attraction between the molecules or particles of solute and solvent.

Heterogeneous solution: It is defined as the mixture of two or more phases.

Solvation: It is defined as the process of interaction of solvent molecules with solute particles to form aggregates. When water is used as solvent, it is called as hydration or aqutation.

Remember:

Extent of dissolution of solute in solvent to form homogenous solution depends on nature of solute and solvent.

General rule for solubility is "Like dissolves like" i.e. polar solutes are soluble in polar solvents.

E.g. NaCl in water.

or non-polar solutes are soluble in non-polar solvents. E.g. Iodine in CCl_4

Explain: Water is called universal solvent.

- 1) It is polar in nature hence it dissolves most of polar solutes.
- 2) It has high -dielectric constant. Hence, it reduces the force of attraction between ions of solute and offers them to remain apart.
- 3) Thus, it acts as good medium for greater ionization of the solutes hence it is called as universal solvent.

Types of solution:

No.	Solute	Solvent	Examples
1	Solid	Solid	Alloys like brass, bronze, copper in gold etc.
2	Liquid	Solid	Amalgams of mercury with metal
3	Gas	Solid	Hydrogen gas in palladium metal, pumice stone
4	Solid	Liquid	Iodine in CCl_4 benzoic acid in C_6H_6 , sugar in water
5	Liquid	Liquid	Ethanol in water
6	Gas	Liquid	Oxygen, carbon dioxide in water
7	Solid	Gas	Iodine in air
8	Liquid	Gas	Chloroform in nitrogen
9	Gas	Gas	Air, mixtures of non reacting gases

Aqueous solution: The solution in which water is used as solvent is called as aqueous solutions.

Non-aqueous solutions: The solution in which solvent other than water is used is called as non-aqueous solution.

Concentration of solutions: It is defined as the amount of solute dissolved in specific amount of solvent.

Dilute solutions: The solutions containing relatively less amount of solute are called as dilute solutions.

Concentrated solution: The solution containing relatively more amount of solute is called as concentrated solution.

Different methods of expressing the concentration of solution -

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

Formula:

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

Where

Mass of solution = Mass of solute + Mass of solvent

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

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

Formula:

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

Note:

- Used when both the components of solution are in liquid phase.
- Total volume of solutions is not equal to sum of volumes of solute and solvent as some solute particles occupy empty spaces in voids in structure of liquids.
- Volume is temperature dependent and hence (v/v) changes with temperature.
- (w/v) is mass of solute in grams present in 100 ml of solution.

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

Mathematical expression of x :

For binary solution,

n_1 – number of moles of solvent

n_2 – number of moles of solute

$$\text{mole fraction of solvent } x_1 = \frac{n_1}{n_1 + n_2}$$

$$\text{mole fraction of solute } x_2 = \frac{n_2}{n_1 + n_2}$$

Note:

- Sum of mole fractions of solvent and solute $x_1 + x_2 = \frac{n_1 + n_2}{n_1 + n_2} = 1$
- Sum of mole fraction of all components of any solution is always unity.
- Mole fraction is temperature independent.

- 4) **Molarity (M)** : It is defined as the number of moles of solute present in 1 dm³ (lit) volume of the solution.

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{volume of solution in dm}^3 \text{ or litre}}$$

$$\text{No. of moles of solute} = \frac{\text{Mass of solute in gram}}{\text{Molecular weight in gram}}$$

Note :

- Molarity is expressed in mol dm⁻³
- It depends on temperature as it contains the term volume.

5) **Molality (m):** It is defined as the number of moles of solute dissolved in 1kg of solvent.

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

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

6) **Normality (N):** It is defined as the no. of gram equivalents of solute dissolved in 1 dm³ of solution.

$$\text{Normality (N)} = \frac{\text{No. of gram equivalents of solute}}{\text{volume of solution in dm}^3}$$

Where

- No. of gram equivalent = $\frac{\text{mass of solute in gram}}{\text{Equivalent wt. of solute in gram}}$
- Equivalent wt. of acid = $\frac{\text{Molecular wt of acid}}{\text{Basicity}}$
(Basicity is the no. of moles of H⁺ ions produced by 1 mole of acid)
- Equivalent wt. of Base = $\frac{\text{Molecular wt of Base}}{\text{Acidity}}$
(Acidity is the no. of moles of OH⁻ ions produced by 1 mole of base)
- Equivalent wt of salt = $\frac{\text{Molecular wt of salt}}{\text{Total charge present on cations}}$

Relation between molarity and Normality. $N = n \times M$

Where n = acidity / basicity

(Note: normality is temperature dependent)

7) **Parts per million (ppm):** It is defined as the mass or volume of solute in gram or cm³ per 10⁶ gram of 10⁶ cm³ of the solution.

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

(Note: It can be expressed as mass to mass, mass to volume or volume to volume.)

Solubility of solute in solvent.

Depending on amount of solute present in given volume of solution it is classified into 3 categories.

- 1) Saturated solution
- 2) Unsaturated solution
- 3) Supersaturated solution

Concept of Solubility (Saturated solution)

- When solute (sugar) is added to solvent (water) , it gets dissolved due to attractive force between solute particles and solvent molecules.
- Solute particles are constantly in state of random motion and constantly collide with each other and with solvent molecules.
- Solute particles are held together due to/ by physical forces of attraction.

- If physical forces are not sufficient, dissolved sugar solute crystallizes out.
- If solute is added continuously, Dissolution and crystallization takes place simultaneously.
- At low concentration of solute, rate of dissolution is very high and rate of crystallization is very low.
- With increase in concentration of solute rate of dissolution decreases and rate of crystallization increases.
- At a particular stage, rate of dissolution and rate of crystallization becomes equal and equilibrium is established.
- At this stage solution is called as saturated.
- $\text{sugar(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{sugar solution}$.

Definition:

- **Saturated solution:** It is defined as the solution that contains just the amount of dissolved solute necessary to establish equilibrium between dissolved solute and undissolved solute.
- **Unsaturated solution:** A solution which contains less amount of solute than required for forming saturated solution.
- Note: Equilibrium does not exist between dissolution and crystallization.
- **Supersaturated solution:** A solution which contains excess of solute than required for formation of saturated solution.
- **Solubility-** It is defined as the maximum amount of solute which dissolves completely in given amount of solvent at a constant temperature.
- It is expressed as mol/lit.
- Solubility changes with temperature.

Effect of temperature on solubility of solid solute in liquid solvent.

- Generally solubility of solid in liquid increases with increase in temperature.
- Solubility of solid solute is almost doubled for every rise of temperature by 10°C which is always not true.
- The solubility of solid solute in liquid solvent may be exothermic or endothermic process.
- Depending on nature of process, solubility may increase or decrease by increasing temperature.
- For exothermic process, solubility decreases by increasing temperature while in case of endothermic process, solubility increases with increase in temperature.

Variations of solubility with temperature for some ionic compounds.

- Solubility of NaBr, NaCl, KCl change slightly with temperature.
- Solubility of salts like KNO_3 , NaNO_3 , KBr increases appreciably with temperature.
- Solubilities of Na_2SO_4 decrease with increase in temperature.
- Solubility of NH_4NO_3 being endothermic process increases with increase in temperature.
- **Exceptional behavior:** solubility of CaCl_2 is exothermic process still it is increased when temperature increases.
- By knowing solubility, it is easy to separate individual component from mixture of water soluble salt from aqueous solutions. This process is called as fractional crystallization.
- This technique can be used if the substance is highly soluble at higher temperature and solubility is poor at lower temperature. E.g. separation of pure NaCl from mixture of NaCl and NaBr at 0°C . Separation of 80% dissolved KNO_3 from mixture of KNO_3 and NaNO_3 .

Effect of pressure on solubility of solid solute in liquid solvent.

Solids are incompressible hence change of pressure has no effect on solubility of solids in liquids.

How Solubility of gases in liquids depends on their nature?

- Gases are soluble in liquids including water.
- Being non polar, solubility of gases like oxygen and nitrogen is very low in water.
- CO_2 reacts with water to form carbonic acid and ammonia reacts with water to form ammonium hydroxide, hence CO_2 and NH_3 are more soluble in water.
- HCl is polar; hence its solubility is very high in water.

Effect of change of temperature on solubility of gas in liquid -

- According to Charles's law, volume of given mass of gas increases with increase of temperature.
- Thus volume of given mass of dissolved gas in solution increases with increase of temperature.
- Due to this, solvent in the solution cannot accommodate the gaseous solute and hence gas bubbles out.
- Thus solubility of gas in liquid decreases with increase in temperature.

Adverse effect of increase in temperature on solubility of O_2 .

- Many times, sea water or river water is used as coolant.
- Cold water is taken from sources of water and after removing heat, hot water from plant is released into source of water.
- Due to this temperature increases and solubility of oxygen gas in water decreases.
- This results in difficulty of survival of marine life

Explain why marine life like fish prefers to stay at lower sea level in summer?

- In summer hot day, temperature of surface of water is relatively very high and solubility of oxygen at upper layer is minimum.
- While temperature of water at lower level is much less and hence it contains more amount of dissolved oxygen.
- Due to this, marine life prefers to stay at lower level for their survival.

Effect of change of pressure on the solubility of gases.

- As gases are highly compressible, external pressure affects their solubility.
- Increase in external pressure increases solubility of gas.

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

Mathematical expression

$$S \propto P \quad \therefore S = KP$$

Where S is solubility of the gas in mol/dm^3 P is pressure of the gas in atmosphere.

K is constant of proportionality. i.e. Henry's constant. If $P = 1 \text{ atm}$. $\therefore S = K$

Definition of K and its unit.

K is defined as solubility of gas in mol/dm^3 at 1 atm pressure and at reference temperature.

Note: for several gases, solubility of gas is calculated by using P as partial pressure of gas in the mixture

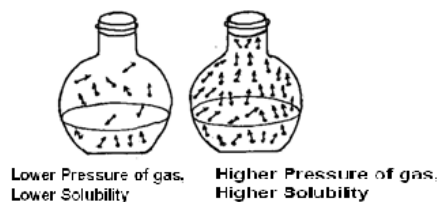


Illustration Of Henry's Law

Explain Henry's law with suitable example.

- When carbonated soft drink beverage bottle is sealed with cap, it is pressurized by mixture of air and CO_2
- Due to high partial pressure of CO_2 , the amount of CO_2 in dissolved state is high in soft drinks.
- When cap is removed external pressure decreases, solubility of CO_2 decreases and excess of CO_2 and air in the bottle escapes out.

Effect of addition of soluble salt on solubility of gases.

The solubility of dissolved gas is reduced by addition of soluble salt to the solution of gas.

E.g. addition of table salt, to carbonated soft drink decreases solubility of CO_2 gas hence it escapes out with effervescence.

Solid solutions - A solid solution of two or more metals or of a metal or metals with one or more non metal is called an Alloy or solid solution.

Name of Alloy	Composition	Properties	Uses
Duralumin	Aluminium, copper, magnesium and manganese.	It is light and strong as steel	It is used in the construction of aircrafts.
Lead hardened by the addition of 10-20% antimony	Lead and 10 to 20% Sb (Antimony)	It is acid resistant	Used for manufacturing lead storage battery plates and bearings, bullets, and shrapnel.
Babbitt metal	Alloy of antimony with tin and copper	it is antifriction	extensively used in machine bearings
Stainless steel	Contains chromium and some nickel.	Hard and strong. It is resistant to corrosion,	Used in cutlery.

spiegeleisen	5 to 20% manganese in iron	very hard	to manufacture rails, safes and heavy machinery
Ferromanganese	70 to 80% manganese and 30 to 20% iron	very hard	to manufacture rails, safes and heavy machinery
Manganin	84% Cu, 12% Mn and 4% Ni	almost zero temperature coefficient of electrical resistance	Used in instruments used for making electrical measurements.
Amalgams.	Mercury with other metals	This property of mercury to form amalgams is used for extracting metals from the ores.	Silver and gold from the ores, dissolve in mercury to form liquid amalgams. Gold and silver are recovered by distilling off mercury.

- In alloys like bronze and lead shot arsenic is used as hardening agent.
- Most of the chromium produced all over the world is used to produce steel alloys
- Aluminium bronze contains Aluminium, copper and small amount of manganese.

Colligative properties: The properties of solutions that depend only on the number of solute particles in solution and not on the nature of the solute particle are called as Colligative properties.

- Colligative properties are used to determine molar masses of non electrolyte solutes.
- The relations derived by measuring colligative properties hold good for dilute solutions, with concentration less than or equal to 0.2M.

Four Colligative Properties

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

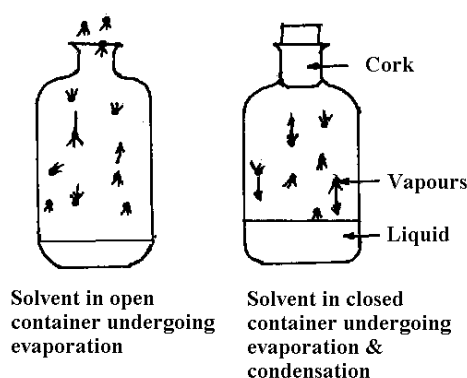
Lowering of vapour pressure of solvent in solution

- All liquids exhibit tendency for evaporation. The gaseous state of a substance is called vapour
- If the intermolecular forces of attraction are weak the liquids evaporate readily and are called volatile liquids. E.g Ethyl acetate is the most volatile liquid. Ethyl alcohol, acetone are also volatile liquids
- Due to strong intermolecular forces of attraction, Lubricating oils are slightly volatile..

Concept of Vapor pressure of liquid

- Liquid escapes from an open vessel by evaporation.
- If the vessel is closed, the process of evaporation continues.

- The molecules of liquid escaping from the surface of liquid remain in the container above the surface of liquid.
- These molecules of vapour are in continuous random motion
- They collide with each other, with the walls of the container and with the surface of the liquid and return to the liquid state. This is reverse of evaporation, called condensation
- After some time interval, equilibrium is established between two phases of the substance, liquid and its vapour. At this stage the rate of evaporation equals the rate of condensation.
- The pressure exerted by vapor at this stage is called as Vapor pressure.
- Vapour pressure of a liquid, increases with the increase of temperature.
- **Note: If the boiling is carried out in an open atmosphere then external pressure is the atmospheric pressure.**

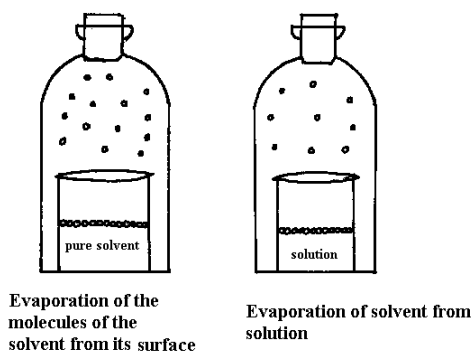


Definition of Vapor pressure of Liquid

- The vapour pressure of a substance is defined as the pressure exerted by the gaseous state of that substance when it is in equilibrium with the solid or liquid phase.

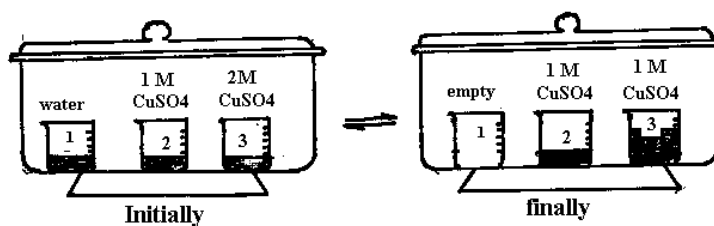
Concept of Lowering of vapor pressure of solvent in solution

- The vapour pressure of a liquid solvent is lowered when a non-volatile solute is dissolved in it to form a solution.
- In case of pure solvent, its surface area is completely occupied by volatile solvent molecules.
- In case of solution of nonvolatile solute, its surface area is not completely available for volatile solvent but it is partly occupied by non volatile solute.
- Hence, rate of evaporation of the solution will be less as compared to that of pure solvent
- Thus vapour pressure of solution is lower than that of the pure solvent.
- **Definition:** The difference between vapour pressures of pure solvent and the vapor pressure of solvent from solution is called vapour pressure lowering.



Describe the experiment for lowering of vapor pressure of solvent due to addition of non-volatile solute.

- Consider three beakers numbered as 1, 2, and 3 containing 100 ml each of pure solvent water, 1M copper sulphate and 2 M copper sulphate solution respectively.
- The three beakers are placed in airtight dessicator, so that at constant temperature, solvent from all the three beakers evaporates and condense and equilibrium is reached.
- **Observations at Equilibrium**
 - Beaker 1 is empty i.e solvent evaporates completely from beaker 1.
 - In beaker 2, conc. Of copper sulphate does not change i.e. volume of solution remains almost same.
 - In beaker 3, condensation of solvent takes place hence volume of solution becomes almost 200 ml and conc. Of solution becomes 1M i.e. almost equal to that of beaker 2.



- **Conclusion of experiment**
 - Vapor pressure of pure solvent water is maximum.
 - Vapor pressure of 1 M copper sulphate is intermediate.
 - Vapor pressure of 2 M copper sulphate is minimum.
- Thus lowering of vapor pressure of solvent takes place due to addition of non-volatile solute.

Mathematical Expression for lowering of vapour pressure

- If p_1^0 is the vapour pressure of pure solvent and p is the vapour pressure of the solution of nonvolatile solute in the same solvent, then $p < p_1^0$ and the lowering of vapour pressure is,

$$\Delta p = p_1^0 - p$$

The relative lowering of vapour pressure: The relative lowering of vapour pressure for the given solution is the ratio of vapour pressure lowering of solvent from solution to the vapour pressure of pure solvent. Thus,

$$\text{Relative lowering of vapour pressure} = \frac{\Delta p}{p_1^0} = \frac{p_1^0 - p}{p_1^0}$$

Raoult's law: The partial vapour pressure of any volatile component of a solution is the product of vapour pressure of that pure component and the mole fraction of the component in the solution.

Derive expression of Raoult's Law for a solution containing both volatile components

- Consider a solution containing two volatile components A_1 and A_2 with mole fraction x_1 and x_2 respectively.

- Let p_1^0 and p_2^0 be the vapour pressures of the pure components A_1 and A_2 respectively.
- According to Raoult's law, the partial pressures, p_1 and p_2 of the two components in the given solution are given by,

$$p_1 = p_1^0 x_1 \text{ and } p_2 = p_2^0 x_2$$

- Total vapour pressure, p_T of solution of two volatile components is the sum of partial vapour pressures of the two components.
- Hence, $p_T = p_1 + p_2 = p_1^0 x_1 + p_2^0 x_2$
- For binary solution, $x_1 + x_2 = 1$ or $x_2 = 1 - x_1$
- Hence, $p_T = p_1^0 x_1 + p_2^0 (1 - x_1)$

$$p_T = p_1^0 x_1 + p_2^0 - p_2^0 x_1 \qquad p_T = p_2^0 + (p_1^0 - p_2^0) x_1$$

Note: The solution which obeys Raoult's law over the entire range of concentration is called an ideal solution. If a solution does not obey Raoult's law, the solution is non-ideal.

Derive Expression of Raoult's law for a solution of non-volatile solute or Derive Expression for relative lowering of vapor pressure of solution containing non-volatile solute.

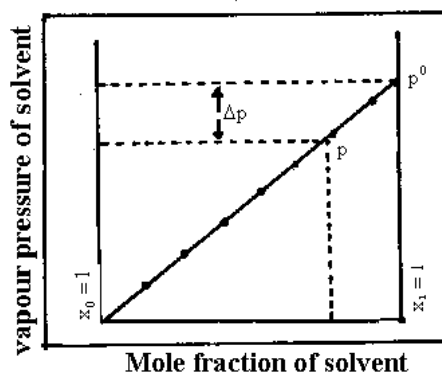
- Consider a solution of two components A_1 and A_2 with the mole fraction x_1 and x_2 respectively.
- In this solution the component A_2 (i.e. solute) is non-volatile, hence it does not evaporate and does not contribute to the total vapour pressure of solution.
- The vapour pressure of pure component A_1 is p_1^0 and that of component A_2 is $p_2^0 = 0$.

$$p_T = p_2^0 + (p_1^0 - p_2^0) x_1$$

$$\text{As } p_2^0 = 0$$

$$p_T = p_1^0 x_1$$

- Thus Vapor pressure of a solution of non-volatile solute is the product of vapour pressure of pure solvent p_1^0 and mole fraction of the solvent, x_1 which is Raoult's law.
- For two component solution, $x_1 + x_2 = 1$. $\therefore x_1 = (1 - x_2)$, where x_2 is mole fraction of non-volatile solute, not equal to zero. Hence, $x_1 < 1$
- Hence Product $p_1^0 x_1$ is always less than p_1^0 . Therefore vapour pressure of solution, $p_T < p_1^0$ which proves that lowering of vapour pressure of solution containing non-volatile solute.



Variation of vapour pressure of solution with mole fraction of solvent in solution

- The lowering of vapour pressure Δp is given by,

$$\begin{aligned}\Delta p &= p_1^0 - p_T \\ &= p_1^0 - p_1^0 x_1 &= p_1^0 (1 - x_1) &\text{But } 1 - x_1 = x_2 \\ \text{Hence, } \Delta p &= p_1^0 x_2\end{aligned}$$

- Lowering of vapour pressure is the product of vapour pressure of pure solvent and mole fraction of non-volatile solute dissolved in volatile solvent to form a solution.
- The lowering of vapour pressure depends on nature of pure solvent and concentration of solute in mole fraction.

The relative lowering of vapour pressure is given by,

$$\frac{\Delta p}{p_1^0} = \frac{p_1^0 - p}{p_1^0} = \frac{p_1^0 x_2}{p_1^0} = x_2$$

Hence, relative lowering of vapour pressure = x_2 (Mole fraction of non-volatile solute)

The above expression proves that the lowering of vapour pressure is a colligative property because it depends on the concentration of non-volatile solute.

Determination of Molar mass of non-volatile solute and relative lowering of vapour pressure:

- Let W_2 g of solute of molar mass M_2 be dissolved in W_1 g of solvent of molar mass M_1 .
- Hence number of moles of solvent, n_1 and number of moles of solute n_2 , in solution are given as,

$$n_1 = \frac{W_1}{M_1} \text{ and } n_2 = \frac{W_2}{M_2}$$

- The mole fraction of solute x_2 is given by,

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{W_2 / M_2}{W_1 / M_1 + W_2 / M_2}$$

- Combine equations

$$\frac{\Delta p}{p_1^0} = \frac{p_1^0 - p_T}{p_1^0} = x_2 = \frac{W_2/M_2}{W_1/M_1 + W_2/M_2}$$

- For dilute solutions, $n_1 \gg n_2$. Hence n_2 may be neglected in comparison with n_1 in equations takes the form.

$$\frac{\Delta p}{p_1^0} = \frac{n_2}{n_1} = \frac{W_2/M_2}{W_1/M_1} = \frac{W_2 M_1}{W_1 M_2}$$

- Knowing the masses of non-volatile solute and the solvent in dilute solutions and by determining experimentally vapour pressure of pure solvent and the solution it is possible to determine molar mass of a non-volatile solute.

Boiling point: Boiling point is defined as the temperature at which the vapour pressure of liquid becomes equal to the atmospheric pressure.

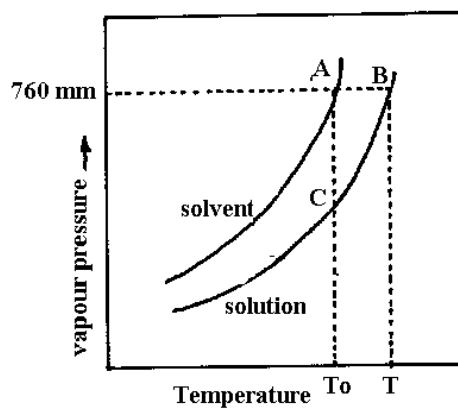
It increases with increase in external pressure. Liquids having greater intermolecular forces have high boiling points.

Concept of Elevation of boiling point

- The vapour pressure of a solution of non-volatile solute is always less than the vapour pressure of pure solvent.
- At the temperature of boiling point of pure solvent, solution will not boil as its vapour pressure is less than that of the vapour pressure of pure solvent which is also equal the external pressure.
- Thus solution will only boil if its vapour pressure is increased upto external atmospheric pressure.
- The temperature must be increased by $\Delta T_b = T - T^0$. Where T is boiling point of solution and T^0 that of pure solvent and $T > T^0$. ΔT_b is elevation of boiling point
- Definition** - Elevation of boiling point is the difference between boiling points of solution and that of pure solvent.

Show graphical representation of elevation of boiling point of solvent in solution or Show Variation of the vapour pressure of pure solvent and solution with temperature.

- The vapour pressure temperature curve of solution is always below the vapour pressure - temperature curve of pure solvent.
- The boiling point of pure solvent is T^0 and that of solution is T .
- The elevation of boiling point ΔT_b is represented by the distance AB . ($\Delta T_b = T - T^0$)
- The lowering of vapour pressure ($p_1^0 - p$) at the temperature T^0 is equivalent to AC .
- The elevation of boiling point is proportional to the lowering of vapour pressure i.e. $\Delta T_b \propto \Delta p$



Vapour pressure temperature curve of pure solvent and solution

Derive the expression to calculate the molecular weight of unknown solute by measuring elevation in boiling point.

- For a dilute solution the elevation of boiling point (ΔT_b) is directly proportional to the molality, m of the solution.
- Thus, $\Delta T_b \propto m$
- $\Delta T_b = K_b m$eqn(1)

Where m is the molality of the solution, K_b is called molal elevation of boiling point constant or ebullioscopic constant.

- If W_2 gram of solute with molar mass M_2 is dissolved in W_1 Kg of solvent then,
- $$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in Kg}}$$

- $$m = \frac{W_2 / M_2}{W_1}$$

- Thus substituting value of m in eqn (1), we get,

- $$\Delta T_b = \frac{K_b W_2}{M_2 W_1} \Rightarrow M_2 = \frac{K_b W_2}{\Delta T_b W_1}$$

Define K_b . State its unit. K_b .

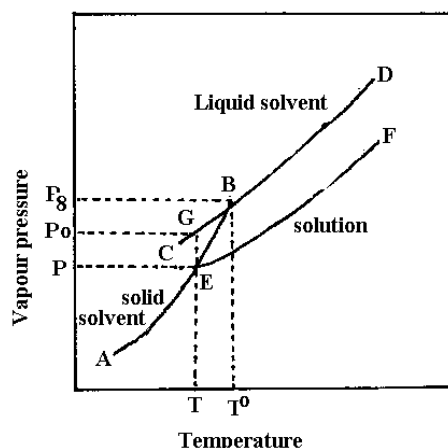
- According to equation $K_b = \Delta T_b / m \Rightarrow \Delta T_b$ is expressed in Kelvin and m in mol kg^{-1} .
- Hence unit of K_b is K kg mol^{-1} .
- For $m = 1$ molal, $K_b = \Delta T_b$.
- **Definition of K_b** - It is the elevation of boiling point produced, when one mole of solute is dissolved in 1 kg of solvent.
- **Value of K_b depends on nature of solvent.**

Freezing point: Freezing point of a liquid is a temperature at which the vapour pressure of solid is equal to the vapour pressure of liquid.

Depression of freezing point: Solution has lower vapour pressure than pure solvent and hence freezes at lower temperature than pure solvent. Thus depression of freezing point is the difference between the freezing point of pure solvent and freezing point of solution containing non-volatile solute.

Show graphical representation of freezing point depression of pure solvent by addition of non-volatile solute.

- AB is the solid-vapour sublimation curve of the solid solvent, CD is the liquid-vapour pressure curve of pure liquid solvent.
- At the freezing point, solid and liquid phases have identical vapour pressures.
- At point B, the two forms have same vapour pressure and therefore T^0 , the temperature corresponding to B, must be the freezing point of pure solvent.
- When solute is dissolved in the solvent, the vapour pressure of solvent lowered and can no longer freeze at temperature T^0 .
- A new equilibrium is established at point E, where vapour pressure of solvent of the solution and solid solvent becomes identical. It is assumed that solute does not dissolve in solid solvent.
- The temperature T, corresponding to the point E, where the vapour pressure curve of the solution intersects the sublimation curve, is the freezing point of the solution.



Variation of vapour pressure with temperature of pure solvent, solid solvent and solution

- The vapour pressure curve of the solution EF always lies below the vapour pressure curve of pure solvent. Hence intersection of vapour pressure curves of solution and solid solvent can occur only at a point lower than T^0 .
- Therefore any solution of the solute must have freezing point T, lower than that of the pure solvent.

$$\text{Thus } \Delta T_f = T^0 - T$$

- For dilute solutions, of different solutes for a given solvent, ΔT_f varies linearly with concentration irrespective of the nature of the nonvolatile, non electrolyte solute.
- The depression of freezing point is proportional to the lowering of the vapour pressure and hence to the mole fraction of the solute. Thus, for dilute solutions, $\Delta T_f \propto p_1^0 - p$
- Greater the lowering of vapour pressure ($p_1^0 - p$), greater will be the depression of freezing point.

Derive the expression to calculate the molecular weight of unknown solute by measuring depression in freezing point of pure solvent by addition of non-volatile solute.

- Freezing point depression of any solution is directly proportional to the molality of solution. Thus,

$$\Delta T_f \propto m \quad m \text{ is molality of solution}$$

$$\Delta T_f = K_f m \dots \dots \dots \text{eqn(1)}$$

K_f , the proportionality constant called molal depression in freezing point constant or cryoscopic constant or freezing point depression constant.

- If W_2 gram of solute with molar mass M_2 is dissolved in W_1 Kg of solvent then,

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in Kg}}$$

$$m = \frac{W_2 / M_2}{W_1}$$

Thus substituting value of m in equation (1), we get ,

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

Definition of K_f and its unit

- $\Delta T_f \propto m$ m is molality of solution
- If $m = 1$ then $\Delta T_f = K_f$.
- Cryoscopic constant is defined as, the depression of freezing point produced by dissolving 1 mole of solute in 1 kg of solvent (i.e.1 molal solution)
- According to equation, $\Delta T_f = K_f m$, hence, $K_f = \Delta T_f / m$
- Unit of K_f is $K \text{ kg mol}^{-1}$.

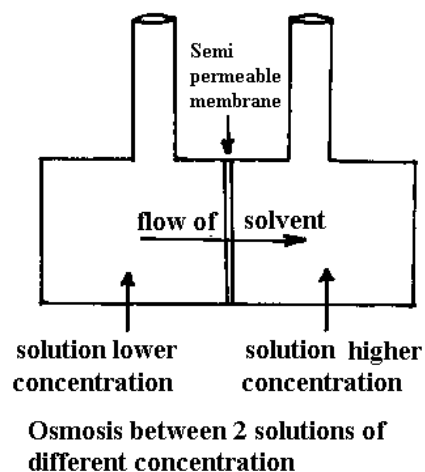
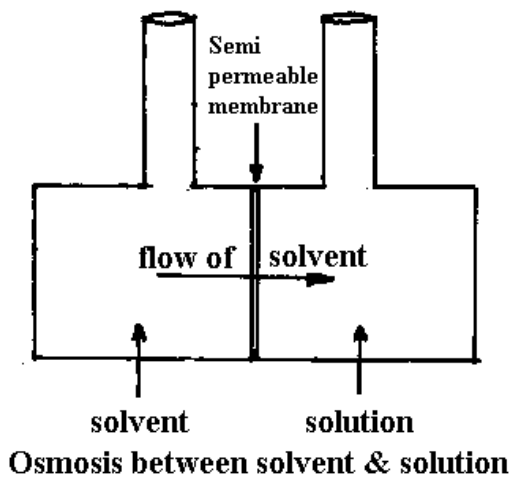
Semi permeable membrane:

- It is a membrane which allows the solvent molecules, but not the solute molecules, to pass through it.
- The thin films of the copper ferrocyanide $\text{Cu}_2[\text{Fe}(\text{CN})_6]$, deposited in pores of porous porcelain pot is the best semi permeable membrane.
- Cellulose, cellulose nitrate, animal bladder, etc. are used as semi permeable membranes.

Osmosis

- When a solution is separated from pure solvent by a semipermeable membrane as shown in figure, the solvent molecules pass through the membrane into the solution and dilute it.

- Similarly, when two solutions of different concentrations are separated by semipermeable membrane then the direction of flow of solvent molecules is from the solution of lower concentration to the solution of higher concentration.
- Due to flow of solvent into the high concentrated solution, the solution gets diluted.
- The flow continues till the concentrations of the two solutions become equal.



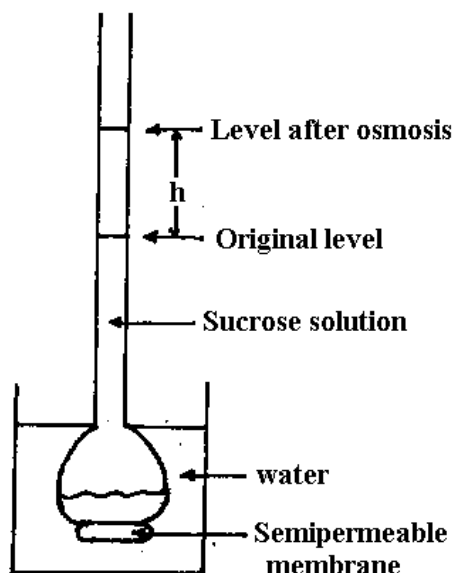
Definition of Osmosis-

The spontaneous and unidirectional flow of solvent molecules through a semi permeable membrane, into the solution or flow of solvent from a solution of lower concentration to the solution of higher concentration through a semi permeable membrane is called osmosis.

Describe the Abbe Nollet Experiment for osmosis

- The apparatus consists of a long stem thistle funnel.
- The mouth of the thistle funnel is closed by semipermeable membrane like pig's bladder.
- Sucrose solution of some concentration is then filled in the thistle funnel.
- The thistle funnel is then placed in beaker containing water in inverted position.
- The net flow of solvent molecules occurs into the solution through the semipermeable membrane.
- Due to this, the original volume of the solution increases and the liquid level of solution rise.
- Hydrostatic pressure is developed due to the liquid column in thistle funnel.
- Due to osmosis, solvent molecules from beaker enter into thistle funnel through semipermeable membrane. The liquid level in the thistle funnel tube rises until the excess pressure so produced is sufficient to stop the flow of solvent molecules. The equilibrium is reached when the hydrostatic pressure of the column matches the osmotic pressure.
- **Osmotic Pressure:** The excess of pressure on the side of solution that stops the net flow of solvent into solution through semipermeable membrane is called osmotic pressure.

Note: The osmotic pressure is not the pressure produced by solution. It exists only when the solution is separated from the solvent by the semipermeable membrane. The resulting osmosis produces an excess pressure (osmotic pressure) in the solution.



Osmosis, Abbe Nollet Experiment

Drawbacks of Abbe Nollet Experiment:

- The entry of the solvent into the solution causes its dilution and concentration changes.

Remedy for Abbe Nollet Experiment:

- The experimental set up must have the arrangement for applying an external mechanical pressure on the solution so that there is no flow of solvent and concentration remains unchanged.
- The external pressure applied to stop osmosis is a measure of osmotic pressure.

Alternative Definition of Osmotic Pressure (π)

- Osmotic pressure of a solution can also be defined as the excess mechanical pressure which must be applied on the side of solution to stop the flow of solvent molecules through semipermeable membrane into the solution.

Types of solution on the basis of osmotic pressure

1. Isotonic solution:

- Two or more solutions exerting the same osmotic pressure are called isotonic solutions.
- For example, $0.05\text{M}(3.0\text{ gL}^{-1})$ urea solution and $0.05\text{M}(17.19\text{ gL}^{-1})$ sucrose solution are isotonic because their osmotic pressures are the same.
- If these solutions are separated by a semipermeable membrane, there is no flow of solvent in either direction.

2. Hypertonic solution:

- A solution having osmotic pressure higher than that of another solution is said to be hypertonic with that solution.
- E.g. 0.1 M urea solution exerts higher osmotic pressure than 0.05 M sucrose solution. Hence, 0.1M urea solution is hypertonic to 0.05 M sucrose solution.
- If these solutions are separated by a semipermeable membrane, the solvent flows from sucrose to urea as sucrose is having low concentration.

3. Hypotonic solution:

- A solution having osmotic pressure lower than that of another is said to be hypotonic solution with that solution.
- For example, 0.05 M sucrose solution has osmotic pressure lower than that of 0.1 M urea solution. Therefore 0.05 M sucrose solution is hypotonic with 0.1 M urea solution.

Osmosis in day today life:

- A raw mango kept in a concentrated salt solution loses water due to osmosis and shrivel into pickle.
- A limp carrot and celery due to water loss into atmosphere can be placed into water making it firm once again. Water moves in carrot due to osmosis.
- People eating lot of salt experience edema i.e. swelling of tissue cells due to water retention in cells.
- The preservation of fruits by adding sugar protects against bacterial action. Due to osmosis, a bacterium on candid fruit loses water, shrivels and dies.
- 0.91 % solution of sodium chloride (called saline water) is isotonic with Human Blood. Thus medicines are mixed with saline water during intravenous injections which prevents blood cells from shrinking or bursting.
- When blood cells are kept in hypertonic solution (5% NaCl), water comes out of the cells and they shrink in size. While when blood cells are kept in hypotonic solution (Distilled water) water flows into the cell and they swell or burst..
- Osmotic pressure is responsible for transporting water upward from soil to top of trees. In plants the leaves of the tree loose water to the atmosphere constantly by transpiration. The solute concentration in leaf fluid increases and water is pulled up by osmotic pressure. In case of some of the tall trees, water reaches to the height of almost 120 meters by osmosis and capillary action.

Laws of osmotic pressure:

- According to the theory, solute molecules in dilute solutions possess kinetic energy and move in random directions in the solution and behave like gas molecules.
- On collision against semipermeable membrane, the solute molecules exert osmotic pressure equal to the pressure, which the solute molecules would exert if it were gas molecules at the same temperature and occupying the same volume as the solution.
- Thus the osmotic pressure could be considered to be due to bombardment of solute particles on semipermeable membrane.
- The osmotic pressure is thus directly proportional to the number of solute particles or the concentration of solute at constant temperature.

State Van't Hoff - Boyle's Law and its mathematical expression.

- At constant temperature the osmotic pressure (π) of a dilute solution is directly proportional to its molar concentration or inversely proportional to the volume of the solution.

$$\pi \propto C \text{ (C is concentration in mol L}^{-1}\text{)(constant T)}$$

$$C = \frac{n}{V}$$

Hence, $\pi \propto \frac{n}{V}$ or $\pi \propto \frac{1}{V}$ for constant n hence, $\pi V = \text{constant}$ or $\frac{\pi}{C} = \text{constant}$

State Van't Hoff - Charle's Law and its mathematical expression.

- The concentration remaining constant; the osmotic pressure of a dilute solution is directly proportional to the absolute temperature.

$$\pi \propto T \quad (\text{constant } C) \quad \text{i.e. } \frac{\pi}{T} = \text{constant}$$

Van't Hoff general solution equation:

Combining van't Hoff Boyle's and Charle's laws,.

$$\pi \propto \frac{T}{V} = \text{constant} \quad \pi V = kT \quad (k \text{ is constant of proportionality})$$

K is called general solution constant. The equation is called van't Hoff general solution equation. It is similar to general gas equation ($PV = RT$).

Value of k is same as R, the gas constant hence,

$$\pi V = RT \quad \text{where } \pi - \text{osmotic pressure}$$

V – volume of solution containing 1 mole of solute

R – gas constant equal to $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ or $0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$

T – absolute temperature

If V is the volume of solution containing n moles of solute, equation becomes,

$$\pi V = nRT \quad \text{or } \pi = \frac{n}{V} RT \quad \text{or } \pi = CRT$$

Where concentration, $C = \frac{n}{V}$, is the number of moles of solute per liter of solution.

Important Note: If π is expressed in Nm^{-2} and volume in m^3 then $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and when π is expressed in atmosphere and volume in dm^3 then $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$

Van't Hoff - Avogadro's law -

It states that two solutions of equal concentrations of different solutes exert same osmotic pressure at the same temperature. **OR**

It can also be, stated as; equal volumes of isotonic solutions contain an equal number of solute particles at the given temperature.

For a given solution, $\pi V = n RT$

$$\pi_1 V_1 = n_1 RT_1 \dots \dots \text{for solution 1}$$

$$\pi_2 V_2 = n_2 RT_2 \dots \dots \text{for solution 2}$$

- Where, n_1 and n_2 are the numbers of moles of the solutes in V_1 and V_2 liters of the solutions respectively. If $\pi_1 = \pi_2$, $T_1 = T_2$ and $V_1 = V_2$ then from equations, $n_1 = n_2$
- Since, numbers of moles are equal; numbers of molecules are also equal.

Abnormal molecular masses:

- Dilute solution of non-electrolytes like urea, glucose, etc. exhibit colligative properties like lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure.
- In dilute solutions of non electrolytes in aqueous or nonaqueous solvents, the solute remains in normal molecular condition and **DOES NOT** undergo either dissociation or association.
- The solution of nonelectrolytes does not conduct electricity. The colligative properties of solutions of nonvolatile, nonelectrolyte solutes depend on actual number of solute particles present in the solution.
- Hence, Colligative properties \propto Actual number of solute particles present in solution.
- Molecular masses of nonvolatile, nonelectrolyte solutes from dilute solutions can be determined by using the value of colligative property. From these equations, it is observed that colligative property is inversely proportional to molecular mass of solute. This molecular mass is theoretical molecular mass of solute.
- In case of solutions of electrolytes, value of observed colligative properties is either exceptionally higher or lower than the theoretically expected value of colligative property exhibited by solution of non-electrolyte solute of same concentration.
- This is because the electrolyte solute i.e. the solute of acid, base or salt when dissolved in solvent can undergo dissociation or association.
- In case of dissociation of solute, the number of particles in the form of ions is more than actually dissolved. As the no. of particles increases the value of colligative properties also increases.
- In general if solute molecules undergoes dissociation producing 2, 3, 4 ions, the observed molecular mass becomes $1/2$, $1/3$, $1/4$ etc. of the theoretical molecular mass of electrolyte solute.
- In case of some solutes, two or more molecules associate together to produce large aggregate molecules. Because of this, effective number of particles of solute in the solution decreases
- Due to association, observed molecular mass becomes double, triple of the theoretical molecular mass and so on.
- In general, observed, lower molecular masses of electrolyte solutes are due to dissociation of solute molecules or observed higher molecular masses of solutes in nonaqueous solvents are due to association/polymerization and are called abnormal molecular masses.

Explain that how the value of colligative property depends on dissociation of electrolyte solutes by taking suitable example.

- Consider the colligative property, depression of freezing point. (Applicable for other colligative property also)
- Depression in freezing point of solvent by addition of solute is calculated by $\Delta T_f = K_f m$
- K_f For water is $1.86 \text{ K kg mol}^{-1}$ and $K_f = \Delta T_f / m$. Thus theoretical value of K_f is 1.86.
- The ratio of $\Delta T_f / m$ for 0.05 molal aqueous solutions of non electrolytes and electrolytes are experimentally determined and are listed in table.

Experimental or observed values of $\Delta T_f / m$ for different solutes in aqueous solutions are

Solute	Glucose	HCl	NH_4Cl	CoCl_2
$\Delta T_f / m$	1.862 = 1.86×1	3.635 = 1.86×2	3.617 = 1.86×2	5.204 = 1.86×3

The observations from the table are as follows

- The non electrolyte solute glucose neither associates nor dissociates in solution. As the number of solute particles are not changed, the value of $\Delta T_f / m$ which is the theoretical value of K_f is equal to $1.86 \text{ K kg mol}^{-1}$ of solvent water.
- Electrolytic solutes when dissolved in solvent dissociate to produce multiple numbers of ions/particles.
- Due to dissociation of solute, number of particles of solute increases and hence the value of colligative property also increases and thus observed that $\Delta T_f / m$ is approximately equal to integral multiple of K_f value.

The value of integral is equal to total number of ions produced on dissociation as follows.

1. $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$; 2 particles; $\Delta T_f / m = 2 \times 1.86 \text{ K mol}^{-1} \text{ kg}^{-1}$
 2. $\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$; 2 particles; $2 \times 1.86 \text{ K mol}^{-1} \text{ kg}^{-1}$
 3. $\text{CoCl}_2 \rightarrow \text{Co}^{2+} + 2\text{Cl}^-$; 3 particles; $3 \times 1.86 \text{ K mol}^{-1} \text{ kg}^{-1}$
- $\Delta T_f / m = K_f$ Value observed in case of solutions of electrolytes may not be exactly double or triple to that of theoretical K_f value observed in case of solutions of nonelectrolyte solute.
 - The value fluctuates with degree of dissociation of solute in solution.

Explain that how the value of colligative property depends on association of solutes by taking suitable example.

- In some non-polar solvents, two or more molecules of solute associates to form bigger molecules.
- For example, in benzene solutes like acetic acid, benzoic acid etc. associate to form dimmers.
- This association is due to the hydrogen bonding between these molecules.



- Hence numbers of solute particles are reduced to half. And thus value of colligative property also decreases.
- Observed molecular masses of these species in above cases are almost twice the expected values in dilute solution.

Van't Hoff factor

- Van't Hoff factor is defined as the ratio of observed colligative property to the theoretical colligative property

$$i = \frac{\text{observed Colligative Property}}{\text{theoretical Colligative property}}$$

- The theoretical colligative property can be considered as the observed colligative property of a solution assuming the solute as nonelectrolyte of same concentration
- Thus Van't Hoff factor can also be defined as the ratio of observed colligative property produced by a given concentration of electrolyte solution to the property observed for the same concentration of non electrolyte solution. Therefore,

$$i = \frac{\text{observed colligative property of electrolyte solution}}{\text{observed colligative property of non electrolyte solution of same concentration}}$$

In short,

$$i = \frac{(\Delta p \text{ observed})}{(\Delta p \text{ theoretical})} = \frac{(\Delta T_b \text{ observed})}{(\Delta T_b \text{ theoretical})} = \frac{(\Delta T_f \text{ observed})}{(\Delta T_f \text{ theoretical})} = \frac{(\pi \text{ observed})}{(\pi \text{ theoretical})}$$

But colligative property \propto number of solute particles present in solution

Hence,

$$i = \frac{\text{number of solute particles present in solution (N observed)}}{\text{theoretical number of solute particles due to solution of non electrolyte (N theoretical)}}$$

i.e.
$$i = \frac{n(\text{observed})}{n(\text{theoretical})}$$

Similarly, colligative property $\propto \frac{1}{\text{molecular mass (M)}}$

Hence,
$$i = \frac{M(\text{theoretical})}{M(\text{observed})}$$

Express the mathematical relation between Van't Hoff factor (i) and degree of dissociation (α)

- Consider an electrolyte $A_x B_y$ dissolved in the solvent and it undergoes dissociation into x ions of A^{y+} and of B^{x-} as $A_x B_y \rightarrow xA^{y+} + yB^{x-}$

- Assume that the molality of electrolyte is m when it is dissolved in the solvent i.e. m moles of the electrolyte, A_xB_y is dissolved in 1 Kg of solvent.
- On dissolution solute dissociates. Let α be the degree of dissociation of the solute.

	A_xB_y	$xA^{y+} + yB^{x-}$	
Initial moles	m	0	0
No. of moles dissociated / formed	$m\alpha$	$xm\alpha$	$ym\alpha$
No. of moles at equilibrium	$m - m\alpha$	$xm\alpha$	$ym\alpha$

- The total number of moles, m_t in the solution at equilibrium will be, $m(1-\alpha)$ of A_xB_y and $x(m\alpha)$ moles of A^{y+} ions and $y(m\alpha)$ moles of B^{x-} ions.

$$\begin{aligned} \text{Hence, } m_t &= m(1-\alpha) + x(m\alpha) + y(m\alpha) \\ &= m[(1-\alpha) + \alpha x + \alpha y] \\ &= m[1 + (x+y-1)\alpha] \end{aligned}$$

It is convenient to represent the total number of ions produced by dissociation of one molecule of solute A_xB_y i.e. $x+y$ by n' . Hence, $x+y = n'$

$$\text{Therefore, } m_t = m[1 + (n'-1)\alpha]$$

$$\text{Now, Vant Hoff factor, } i = \frac{\text{observed number of moles}}{\text{theoretical number of moles}}$$

$$= \frac{m_t}{m} = \frac{m[1 + (n'-1)\alpha]}{m} \quad \text{Hence, } i = [1 + (n'-1)\alpha]$$

$$\text{The degree of dissociation, } \alpha = \frac{i-1}{n'-1}$$

$$\text{since } i = \frac{M(\text{theoretical})}{M(\text{observed})} = [1 + (n'-1)\alpha]$$

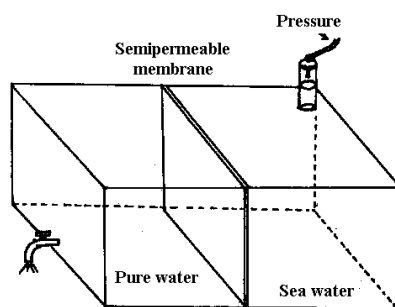
Hence, degree of dissociation $\alpha = \frac{M(\text{theoretical}) - M(\text{observed})}{M(\text{observed})(n'-1)}$

Hence, it is possible to determine degree of dissociation of electrolyte by determining experimentally $M(\text{observed})$ and by measuring experimentally any one of the colligative properties.

Desalination:

- Probably due the greenhouse effect, every body is facing a problem of shortage of water.
- Hence attempts are made to procure drinking water by removing salts from sea water by a process called as Desalination by reverse osmosis.
- Ocean is a large stock of sea-water containing almost 1.5×10^{21} L of water. It contains 3.5 % (w/w) of dissolved salts, mainly sodium chloride.
- Drinking water is produced by using this process.

Concept of Reverse Osmosis:



Purification of sea water by reverse osmosis

- Reverse osmosis is the flow of solvent from high concentrated solution to low concentrated solution.
- In this process, high pressure is applied to force water from concentrated aqueous solution like sea water to pure water side through semi-permeable membrane.
- The osmotic pressure of sea-water is 30 atm. Hence if the pressure on the solution side is greater than 30 atm. Osmosis stops and reverse osmosis starts.
- Due to this solvent from sea water enters the other side of pure water.
- **Note:** The method can be used by using semipermeable membrane which withstands high pressure over prolonged period. By using this method, about 10 million litres of fresh water is produced every day from sea water.