EDUCATALYSTS

Class(12th)

Introduction to Solutions

INTRODUCTION

☺ Homogeneous mixture of two or more substances whose composition vary within certain limits is known as **True Solution**. Eg: Salt in water, sugar in water.

In a homogeneous mixture composition is same throughout the mixture.

☺ A binary solution contains two components-solute and solvent only.

Solute

☺ The component that is present in a lesser amount or the component that loses its physical state (not always) (or) dissolved substance (or) dispersed phase.

Solvent

☺ The component that is present in a greater amount or the component that retains its physical state or dispersion medium (or) dissolving medium.

PROPERTIES OF SOLUTION

☺ It is a homogeneous mixture.

☺ Formation of solution is only a physical change but not a chemical change.

☺ Solute cannot be separated from solution by filtration.

☺ The properties of a solution like density, vapour pressure, boiling point depend on relative amount of solute and solvent.

☺ Variables like pressure, temperature and composition may affect the properties of the solutions.

☺ The effect of pressure on solid solutions is negligible.

TYPES OF SOLUTION

Based on Physical States of Matter

Types of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

— KEY NOTE —

Gases on intermixing produce true solution.

METHODS OF EXPRESSING CONCENTRATIONS OF SOLUTIONS

The quantity of solute present in definite quantity of the solution relative to the solvent is known as **Concentration of solution** or **strength of solution.**

Standard Solutions: The solution whose concentration is known.

Dilute Solution: The solution containing relatively smaller quantity of solute compared to that of solvent.

Concentrated Solution: The solution that contain excess solute, in a fixed quantity of the solution.

Weight of Solution = Volume of the solution × density of solution
$$(W = V \times d)$$

There are several ways by which we can calculate the concentration of solution:-

(i) Percentage(%)

(a) Mass Percentage (w/w): It is defined as weight/mass of solute present in 100 g of solution.

$$\% \ w/w = \frac{weight \ of \ solute \ (g)}{weight \ of \ solution \ (g)} \times 100 = \text{weight of solute/100 g of solution.}$$

☺ It does not change on changing temperature.

Ex. 10% w/w urea solution = 10 gm of urea is present in 100 gm of solution.

= 10 gm of urea is present in 90 gm of water.

(b) Mass by Volume percentage (w/v): It is mass of solute dissolved in 100 ml of solution.

% w/v = wt. of solute/100 mL of solution

$$\% \ w/v = \frac{gram \ of \ solutes}{vol.of \ solution \ in \ mL} \times 100$$

☺ It changes on changing temperature.

Ex. 10% (w/v) urea solution. = 10 gm of urea is present in 100 mL of solution.

But not 10 gm of urea present in 90 ml of water

for dilute solution : vol. solution = vol. solvent.

(c) Volume Percentage (v/v)

If both solute & solvent are liquids = volume in (mL) of solute per 100 mL of solution.

$$V\% = \frac{Volume \ of \ component}{Total \ volume \ of \ solution} \times 100$$

Ex. 10% v/v ethanol aq solution = 10 ml of ethanol in 100 ml of solution.

≠ 10 ml of C_2H_5OH in 90 ml of H_2O

(ii) Strength of solution

Weight of solute (in gram) in a per litre (1000 mL) of solution.

Strength

☺ Weight of solute (in grams) dissolved in per litre of solution . (g/litre)

Strength = Equivalent weight × Normality

Solutions

(iii) PPM (Parts per Million)

☺ It is the mass of the solute present in million (10^6) parts by mass of the solution

$$ppm = \frac{Mass\ of\ solute \times 10^6}{Mass\ of\ solution}$$

(iv) Molarity (M):

☺ It is number of gram moles of solute dissolved per litre of solution.

Unit = Moles/litre

☺ Molarity decreases with increase in temperature.

$$M = \frac{n}{V_{Litre}}$$

Where, n = number of moles of solute, V= Volume of Solution in litres.

n = VM

$$M = \frac{Wt}{M.Wt} \times \frac{1}{V_{lit}}$$

$$M = \frac{W}{M.Wt} \times \frac{1000}{V_{ml}}$$

(v) Normality (N)

☺ It is number of gram equivalents of solute dissolved per litre of solution.

Unit = gm. equivalents / litre

☺ Normality decreases as temperature increases.

$$N = \frac{No.\ of\ gm\ equivalents\ of\ solute}{volume\ of\ solution\ in\ litres}$$

$$N = \frac{W}{E.W} \times \frac{1}{V_{lts}}$$

$$N = \frac{W}{E.W} \times \frac{1000}{V_{ml}} \ ; \quad W = \frac{N \times EW \times V}{1000}$$

— KEY NOTE —

When a solution is diluted or two solutions of different substances react, then $V_1N_1 = V_2N_2$

Equivalent Weight (E)

☺ It is the number of parts by weight of a substance that combine or displace 1.008 parts by weight of hydrogen or 35.5 parts by weight of chlorine or 8 parts by weight of oxygen.

It is represented by E.

It is a relative value, no units.

Equivalent weight expressed in grams is known as gram equivalent weight or gram equivalent.

Number of gram equivalents = $\dfrac{Weight\ of\ the\ substance\ in\ gms}{Gram\ equivalent\ weight}$

Equivalent weight of Acids

$$E_{acid} = \frac{M\ Wt}{basicity}$$

Basicity is the number of replaceable hydrogen atoms by metal ions in a molecule of an acid.

Equivalent weight of Base

$$E_{base} = \frac{M.wt}{acidity}$$

☺ Acidity is the number of hydroxyl groups present in a molecule of the base.

— KEY NOTE —

Relation between Molarity and Normality

• M×M.wt. = N × E.W

$$N = M \times \frac{M.W}{EW}$$

Gram molecular wt = nGram equivalent wt

Where n = valency (or) Basicity (or) acidity (or) number of electrons transferred.

(vi) Molality (m)

☺ It is the number of gram moles of solute dissolved per kg of solvent.

☺ Unit is Moles / kg of solvent.

It is a standard method of expressing concentration while molarity is a convenient method of expressing concentration.

$$m = \frac{n}{W_{Solvent(in\ Kg)}}$$

$$m = \frac{W}{M.wt} \times \frac{1}{W_{solvent\ in\ Kg}}$$

$$m = \frac{W}{M.W} \times \frac{1000}{W_{Solvent\ in\ Gms}}$$

(vii) Mole Fraction(x)

It is ratio between number of moles of one particular component to the total number of moles of all the components of solution.

It has no Unit.

$$x_2 = \frac{No.\ of\ moles\ of\ solute(n_2)}{Total\ no.\ of\ moles\ in\ solution(n_1 + n_2)}$$

— KEY NOTE —

Molality, mole fraction and mass fraction do not change with temperature

Train Your Brain

Q. If we have 6% w/w urea solution with density 1.060 gm/mL. then calculate its strength in g/L.

Ans. 6 g in 100 gm solution.

$$6 g \ in \ \frac{100}{1.060} \ mL$$

$$\frac{100}{1.060} mL \rightarrow 6 \ gm$$

$$\therefore 1000 mL = \frac{6}{100} \times 1.060 \times 1000 = 10.6 \times 6 = 63.6$$

Q. Calculate molality of 1.2 M H_2SO_4 solution

If its $\rho = 1.4$ gm/mL

Ans. Molality $= \dfrac{(molarity) \times 1000}{100 \times d - (molarity) \times M_{wt}}$

$$Molality = \frac{1.2 \times 1000}{1000 \times 1.4 - 1.2 \times 98} = 0.935$$

Q. If we have 10 molal urea solution calculate

Mole fraction of urea in this solution & also calculate % w/w of urea. (MW = 60)

Ans. (i) 10 moles urea in 1000 gm of water

$$X_{urea} = \frac{10}{10 + \frac{1000}{18}} = \frac{10}{65.55} = 0.152$$

% w/w weight of urea $= \dfrac{10 \times 60}{10 \times 60 + 1000} \times 100\% = 37.5\%$

(viii) Formality (F)

☺ This is the concentration unit for ionic compounds that dissolve in a polar solvent to give vapour pair of ions. This represents number of gramformula - weight of the substance dissolved per litre of the solution. It is almost the same as molarity. It describes the solute that is mixed in a liquid rather than the solute present in solution after the dissolution process.

$$Formality = \frac{moles \ of \ substance \ added \ to \ solution}{volume \ of \ solution \ (in \ litres)}$$

SOLUBILITY

Solubility of Solid in Liquid

☺ The amount of solute that is dissolved in 100g of a solvent to form a saturated solution at a given temperature is known as the solubility of solute.

Unsaturated Solution

☺ A solution in which more solute can be dissolved without increasing temperature is called an unsaturated solution.

Saturated Solution

☺ A solution in which no more solute can be dissolved further at a given temperature is called a saturated solution.

☺ The maximum amount of a solute that can be dissolved in a given amount of solvent (generally 100g) at a given temperature is termed as its "**solubility**" at that temperature.

☺ In a saturated solution there exists a dynamic equilibrium between the undissolved and dissolved ions or molecules in solution.

At equilibrium

Rate of dissolution $\Longleftrightarrow$ Rate of crystallization

☺ A supersaturated solution is metastable

Factors influencing solubility of solids:

(a) Temperature

☺ If the dissolution, is endothermic ($\Delta H_{sol} > 0$) the solubility increases with increase in temperature e.g. $NaNO_2$, KNO_3, NaCl

If the dissolution process is exothermic ($\Delta H_{sol} < 0$), solubility is decreasing with increasing in temperature.

(b) Pressure

☺ It has no significant effect on solubility because solids and liquids are highly incompressible.

(c) Nature of Solute / Solvent (solubilities of ionic solids)

☺ The smaller the value of lattice energy and more is the value of heat of hydration more is the solubility of ionic compounds.

Ionic solids dissolve more in a solvent having high dielectric constant

Solubilities of Molecular Solids

(Non-Ionic Solids)

☺ Molecular solids containing polar groups (e.g. OH) are soluble in polar solvents like water, methanol etc. Others are soluble in non polar solvents.

Solubility of Gases in Liquids

☺ It is generally expressed in terms of absorption coefficient which is defined as the volume of the gas in ml which can be dissolved by 1ml of a polar solvent at the temperature of the experiment at 1 atmospheric pressure.

Absorption coefficient of some gases at 20°C

Factors Influencing the Solubility of a Gas

Nature of Gas

☺ Easily liquifiable gases are more soluble. e.g. CO_2 is more soluble than O_2 and H_2

Nature of Solvent

☺ Gases that are capable of forming ions in aqueous solution are more soluble in water than in other solvents.

eg. HCl, NH_3 etc.

Temperature

☺ Solubility decreases with rise of temperature at constant pressure.

Pressure of the Gas

Henry's law: The mass of a gas dissolved per unit volume of solvent is proportional to the pressure of the gas at constant temperature.

Solutions

- $m \propto p$ or $m = K_H P$, where K_H is Henry's constant

- The most commonly used form of Henry's law states that the **partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution"** and is expressed as $p = K_H x$, here K_H is the Henry's law constant.

  Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

  Table: Value of Henry's Constant for Different Gases

Gas	Tempera-ture / K	K_H/ Kbar	Gas	Temperature / K	K_H/kbar
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	Formaldehyde	298	1.83×10^{-5}
N_2	303	88.84	Methane	298	0.413
O_2	293	34.86	Vinyl chloride	298	0.611

Limitations of Henry's Law

(i) pressure is not very high and temperature is not very low

(ii) Gas not highly soluble

(iii) Gas should not form any compound with solvent

(iv) Gas should not undergo dissociation

Application of Henry's law

- To increase solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure

- 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 cop 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.

| VAPOUR PRESSURE OF LIQUID SOLUTION

The pressure exerted by vapour over a liquid when they are in equilibrium with each other is known as vapour pressure.

- Vaporization increases with surface area and temperature.

- Vapour pressure is independent of surface area.
  Vapour pressure varies exponentially with temperature.

- When temperature is increased KE of molecules increases, more number of molecules convert to vapour form and more will be the vapour pressure.

- The vapour pressure of a liquid is called **saturated vapour pressure**, because the atmosphere over liquid is saturated with vapour of the liquid, exerts pressure on the liquid.

- The vapour pressure of water is known as **aqueous tension**.

Boiling Point

- Volatile liquids have high Vapour Pressure and low Boiling Point.
  Eg: - Ether, Methyl alcohol, acetone, benzene, Carbon tetrachloride, Carbon disulphide

- Non volatile liquids have low vapour pressure and high boiling point.
  Eg: - H_2O, Aniline, Nitrobenzene

Vapour Pressure of Solid-Liquid Solutions

Raoult's Law for non Volatile Solute

- *The relative lowering of vapour pressure of a dilute solution containing a non-volatile solute is equal to mole fraction of solute.*

  $$\frac{P^0 - P}{P^0} = x_2 \qquad \frac{P^0 - P}{P^0} = \frac{n_2}{n_1 + n_2}$$

  for very dilute solutions

  $$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1} \implies \frac{P^0 - P}{P^0} = \frac{w}{m} \times \frac{M}{W}$$

  Where P^0 = VP of pure solvent

  P – V.P of pure solution

  w = wt. of solute

  m = M.Wt of solute

  W = Wt. of solvent

  M = M.Wt of solvent

Vapour Pressure of Liquid-Liquid Solution

Raoult's Law for volatile Solute

- *The partial pressure of a volatile component of a solution is directly proportional to its mole fraction in solution at any temperature.*

  $P_A \propto X_A$ and $P_B \propto X_B$ and

  $P_A = P_A^0 \cdot X_A, P_B = P_B^0 \cdot X_B$

  Where P_A – partial pressure of component A,

  P_A^0 – vapoure pressure of component A in pure form,

  X_A – mole fraction of component A in solution

  $P_T = P_A + P_B$

  $P_A = \gamma_A P_T$

  $P_B = \gamma_B P_T$

  Where, γ_A and γ_B are the mole fraction of components A and B in vapour phase respectively.

Particle concentration in Solution

- Molar concentration of solution × number of ions formed from one molecule of Solute

  Eg: - (1) In 0.01M Aqueous solution of $Al_2(SO_4)_3$

  $\left[Al^{3+} \right] = 0.02; [SO_4^{2-}] = 0.03$ M

  Total particle concentration = 0.05M

  Particle concentration of 0.01M glucose solution is 0.01M

  — KEY NOTE —

  - LVP ∝ particle concentration
  - $VP \propto \dfrac{1}{particle\ concentration}$

Limitations of Raoult's Law

☹ It is applicable for very dilute solutions only.

☺ It is applicable for dilute solutions containing non-volatile solute only.

☹ It is applicable for solutions containing solutes, which neither associate nor dissociate.

☹ It is applicable for ideal solutions only.(Solutions in which solute and solvent do not have Interaction).

AN IDEAL SOLUTION & NON IDEAL SOLUTION

(1) The solution that obey Raoult's law at all temperatures and concentrations is known as ideal solution.

(2) $\Delta H_{mix} = 0$ i.e. no heat is evolved or absorbed when components are mixed to form the solution.

(3) $\Delta V_{mix} = 0$ i.e. no change in volume. In ideal solution the A -B intermolecular interactions are the same as A -A and B -B inter molecular interactions
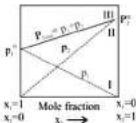

Fig.: The plot of vapour pressure and mole fraction of an ideal solution at constant temperature

In an ideal solution of two components A_2 and B_2, all interactions, i.e. (A -A, B -B and A -B) must be identical.

☺ Two liquids on mixing will form an ideal solution if following conditions be satisfied:

(i) Both have similar structures

(ii) Both have similar molecular sizes

(iii) Both have identical intermolecular forces strictly there is no attraction and repulsions

The following pairs almost behave as ideal solutions:-

(a) Benzene and toluene

(b) Ethyl bromide and ethyl chloride

(c) n - Heptane and n- hexane

(d) Chlorobenzene and bromobenzene

(e) Ethyl iodide and ethyl bromide.

Non-ideal Solutions

(1) Solutions which do not obey Raoult's law is known as non ideal solution

(2) $\Delta H_{mix} \neq 0$

(3) $\Delta V_{mix} \neq 0$

Type of non ideal solutions:

They are of two types

(I) Showing Positive Deviations from Raoult's law

For such solutions

(a) A- B inter - molecular interactions are weaker than A - A and B -B intermolecular interactions

(b) ΔH_{mix} is + ve & ΔV_{mix} is + ve

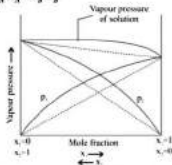(c) $P_{total} > P_A^o \cdot x_A + P_B^o \cdot x_B$

Fig.: A solution that shows +ve deviation from Raoult's Law

Examples:

(i) Carbon tetrachloride +benzene

(ii) Carbon tetrachloride + chloroform

(iii) Carbon tetrachloride + Toluene

(iv) Acetone + Carbon disulphide

(v) Acetone +Ethyl alcohol

(vi) Acetone + Benzene

(vii) Methyl alcohol + Water

(viii) Ethyl alcohol + Water

(II) Showing Negative Deviations From Raoult's Law

For such solutions

(a) A-B intermolecular interactions are stronger than A-A and B-B intermolecular interactions

(b) ΔH_{mix} is –ve & ΔV_{mix} is –ve

(c) $P_{total} < P_A^o \cdot x_A + P_B^o \cdot x_B$

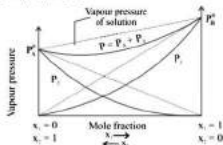**Fig.:** A solution that show negative deviation from Raoult's Law

Examples:

(i) Chloroform + Acetone

(ii) Chloroform + Benzene

(iii) Chloroform + Diethyl ether

Solutions

(iv) Acetone + Aniline

(v) HCl + Water

(vi) HNO_3 + Water

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 eg. Rectified spirit (ethanol 95.5% + H_2O 4.50%) constant boiling point 351.15 K.

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.

eg. Water & HNO_3 (HNO_3 68% + H_2O 32%) constant boiling point 393.5K

COLLIGATIVE PROPERTIES

The properties of dilute solutions that depend on the number of particles (ions or molecules) of the solute dissolved in the solution are called **colligative properties**.

1. Relative lowering of Vapour Pressure

☺ Ostwald's dynamic method is based on the measurement of RLVP of a solution due to addition of a non volatile solute.

Lowering of Vapour Pressure

☺ When a non volatile solute is added to a solvent, the vapour pressure decreases.

☺ In a solution, the surface is not only occupied by solvent molecules but also by solute molecules.

☺ The number of molecules of solvent present on surface are relatively less in solution than that of pure solvent as some solvent molecules on the surface are displaced by solute molecules.

☺ The number of molecules converting to Vapour form are less (vaporization is less). Therefore vapour pressure is less.

☺ RLVP as per Raoult's law, is equal to the mole fraction of solute

$$\frac{P^o - P}{P^o} = x_s$$

Where x_s = mole fraction of solute; $P_o - P$ is lowering of vapor pressure.

$$\frac{P^o - P}{P^o} = \frac{n_s}{n_o + n_s}$$

$$n_s = \frac{a}{M} ; n_o = \frac{b}{W}$$

For dilute solutions $n_s < n_o$

$$\frac{P^o - P}{P^o} = \frac{a}{M} \times \frac{W}{b} \quad \text{or} \quad M = \frac{a \times W}{b} \times \frac{P^o}{(P^o - P)}$$

Train Your Brain

Q. Dry air was passed through a solution of 5 gm of a solute in 80 gm of water & then it is passed through pure water loss in wt. of solution was 2.50 gm & that of pure solvent was 0.04 gm. Calculate M.W. of solute.

Ans. $\dfrac{P - P_s}{P_s} = \dfrac{\text{loss in wt.of solvent}}{\text{loss in wt.of solution}}$

$$\Rightarrow \frac{P - P_s}{P_s} = \frac{0.04}{2.50} = \frac{5}{M} \cdot \frac{18}{80}$$

$$M = 70 \text{ g mol}^{-1}$$

2. Elevation in Boiling point

☺ The temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure (i.e., one atmosphere) is known as the **boiling point of the liquid.**

☺ The vapour pressure (P) of a dilute solution of the non-volatile solute is less than the vapour pressure of the pure solvent (P^o) in which the non-volatile solute is dissolved.

☺ Boiling point of solution (T) is greater than the boiling point of solvent (T^o)

$$(T - T^o) = \Delta T_b, \text{ where } \Delta T_b \text{ is elevation of Boiling point.}$$

☺ For dilute solution elevation of boiling point (ΔT_b) is directly proportional to the molal concentration of the solute in a solution.
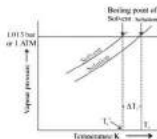

Fig.: The vapour pressure curve for solution lies below the curve for pure water

☺ ΔT_b and K_b are related by the equation

$$\boxed{\Delta T_b = K_b \times m} \quad \text{or} \quad \boxed{\Delta T_b = K_b \times \dfrac{a}{M} \times \dfrac{1000}{b}}$$

Where, m is molality and Kb is molal elevation constant.

☺ The elevation in boiling point observed in one molal solution of a non-volatile solute is called molal elevation constant (K_b) (or) Ebullioscopic constant.

$$K_b = \dfrac{RT_b^{2}}{1000 l_{vap}} = \dfrac{M_b R T_b^{2}}{1000 \Delta H_{vap}}$$

☺ The molal elevation constant of a solvent does not change with the change in the nature of solute dissolved in it.

Train Your Brain

Q. Calculate K_b of water if $L_{vap} = 540$ Cal/gm $T_b = 100°C$

Ans. $K_b = \dfrac{2 \times 373 \times 373}{1000 \times 540} = 0.52\ K\ kg\ mol^{-1}$

3. Depression of Freezing point

☺ **Freezing point** is the temperature at which the solid form of liquid begins to separate out from the liquid. At this temperature solid and liquid will be in equilibrium.

☺ When non volatile solute is dissolved in a solvent the freezing point decreases.

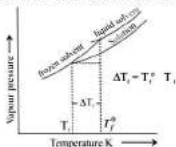☺ For dilute solutions the curves are considered almost linear.

$$\Delta T_f = T_f^{\circ} - T_f$$

Fig.: Diagram showing ΔT_f depression of the freezing point of a solvent in a solution

☺ ΔT_f and K_f are related by the equation

$$\boxed{\Delta T_f = K_f \times m} \quad \text{or} \quad \boxed{\Delta T_f = K_f \times \dfrac{a}{M} \times \dfrac{1000}{b}} \quad \text{or} \quad \boxed{K_f = \dfrac{MRT_f^{2}}{1000(\Delta_{fusing} H^{\circ})}}$$

$\Delta_s H^{\circ}$ = standard enthalpy of freezing.

☺ The depression of freezing point observed in 1 molal solution of a non volatile solute is known as K_f.

☺ K_f depends on chemical nature of solvent but not solute in the solution.

☺ Rast method is used for measuring depression in freezing point

Train Your Brain

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 kcal mol^{-1}, freezing point of solvent = 27°C and R = 2cal mol^{-1} k^{-1}.

Ans. $K_f = \dfrac{MRT_f^{2}}{1000 \Delta H_f} = \dfrac{2 \times 300 \times 300 \times 30}{1000 \times 2700} = 2.00\ K\ kg\ mol^{-1}$

mole fraction of water = 0.8

∴ mole fraction of solute = 0.2

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

∴ $\dfrac{n}{N} = \dfrac{0.2}{0.8} = \dfrac{1}{4} = \dfrac{wM}{mW}$

or $\dfrac{1}{4} = \dfrac{w \times 30}{mW} = \dfrac{w}{mW} = \dfrac{1}{4 \times 30}$

∴ $\Delta T_f = \dfrac{100 \times w \times K_f}{m \times M} = \dfrac{1000 \times 2.0}{4 \times 30} = 16.67$

F.P of solution = 10.33°C

4. Osmosis

The spontaneous flow of the solvent through semipermeable membrane from pure solvent to solution (or) from a dilute solution to concentrated solution is known as **osmosis**.

☺ The membranes which allow to pass only solvent molecules through it but not solute molecules is called semipermeable membrane.

Osmotic Pressure (π)

☺ The hydrostatic pressure produced on the aqueous dilute solution at equilibrium state due to inflow of water when the solution is separated from the water by a semipermeable membrane.

(or)

☺ The pressure required to be applied on the solution to prevent the inflow of solvent into the solution, when the solution is separated from the solvent by a semipermeable membrane.

Vant Hoff's theory of dilute Solutions

According to vant Hoff's, dilute solutions behave as gases. Hence the laws that applicable to gases are also applicable to dilute solutions.

Vant Hoff's Boyle's Law

At constant temperature the osmotic pressure (π) of a dilute solution is directly proportional to its concentration (C)

$$\pi \propto C \qquad (C = mole / litre)$$

$$\pi \propto \frac{1}{V} \qquad \left(\because C \propto \frac{1}{V}\right)$$

$$\pi V = K \quad .....(1)$$

Vant Hoff's Charle's Law

The osmotic pressure (π) of a solution of constant concentration (C) is directly proportional to the temperature in Kelvin Scale (T)

$$\pi \propto T$$

$$\pi = KT \quad ... (2)$$

from (1) and (2) $\pi \propto \dfrac{T}{V}$

$$\pi = S \frac{T}{V}$$

$$\therefore \ \pi = CST \qquad \left(\because \frac{1}{V} = C\right)$$

here S = solution constant

The value of 'S' is similar to the value of 'R' (gas constant)

Hence $\pi V = RT$ for 1 mole

for 'n' mole $\boxed{\pi V = nRT}$

If 'a' is weight of the solute and 'M' is its molecular weight then

$$n = \frac{a}{M}$$

for 'n' moles $\pi V = \dfrac{a}{M} RT$

$$\boxed{\text{(a) } M = \frac{aRT}{\pi V} \qquad \text{(b) } M = \frac{aRTC}{\pi}}$$

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 and 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)

Consider two solutions I and II having n_1 and n_2 moles of the solute in V_1 and V_2 litres of the solution respectively. Let P_1 and P_2 be their osmotic pressures at the same temperature (T)

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

then $\dfrac{n_1}{V_1} = \dfrac{n_2}{V_2}$

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

Hypotonic solutions: Solutions having lower osmotic pressure

Hypertonic Solutions: Solutions having higher osmotic pressure

Plasmolysis

The flow of the liquid from the plant cell when placed in a hypertonic solution is called **plasmolysis**. The plant cell undergoes shrinkage. It is an example to **exo-osmosis**.

Haemolysis

When a plant cell is placed in hypotonic solution then the solvent flows into plant cell. This is known as **Haemolysis**. The plant cell finally bursts. It is an example to **endo-osmosis**.

Train Your Brain

Q. Calculate osmotic pressure of 0.1 M urea aqueous solution at 300 K .

Ans. R = 0.082 lit atm mol K^{-1}

$\pi = CRT$

$\pi = 0.1 \times 0.082 \times 300$

$\pi = 2.46$ atm

Osmotic pressure of very dilute solution is also quite significant so its measurement in lab is very easy.

ABNORMAL MOLAR MASS

☺ Colligative properties are shown by dilute solutions.

☺ Electrolytes undergo ionisation in aqueous solutions, as a result number of particle in the solution increases thus magnitude of colligative properties increases.

☺ Colligative property and molar mass of solute are inversely proportional to each other.

☺ So molar mass of electrolytic solutes determined experimentally is less than true value.

☺ Some solutes when dissolved in solvents may undergo association i.e. solute molecules combine to form dimers or trimers etc.

Association of solute particles

☺ Due to association number of particles in the solution decreases, as a result magnitude of colligative property decreases. So, molar mass of such solute will be higher than true value.

☺ The dissociation result in the increase in total number of particles & thus value of colligative properties of solution will be higher. So, molar mass of such solute will be less than true value.

Van't Hoff Factor (i)

☺ **Van't Hoff** introduced a factor 'i' in the equations to equalise the experimental value and calculated value.

$$i = \frac{\text{experimental value of colligative property}}{\text{Calculated value of colligative property}}$$

$$i = \frac{\text{observed osmotic pressure}}{\text{Calculated osmotic pressure}}$$

Van't Hoff factor and degree of dissociation

☺ For solutes which undergo dissociation: Let a solute on ionisation gives 'n' ions (particles) and 'α' is degree of ionisation at the given concentration, we will have $[1+(n-1)\alpha]$ particles (ions) after ionisation

$$A_n \leftrightarrow nA$$
$$1 \qquad 0$$
$$1-\alpha \qquad n\alpha$$

$$i = \frac{\text{no.of particles after dissociation}}{\text{no.of particles before dissociation}}$$
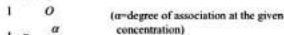
$$i = \frac{[1+(n-1)\alpha]}{1}$$

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

'α' is degree of dissociation or ionisation.

Salt	Van't Hoff Factor i for complete dissociation of solute
NaCl	2.0
KCl	2.0
$MgSO_4$	2.0
K_2SO_4	3.0

Van't Hoff factor & degree of association

☺ For solutes which undergo association

If 'n' molecules of 'A' combine to give A_n, we have

$$nA \rightleftharpoons A_n$$
$$1 \qquad 0$$
$$1-\alpha \qquad \dfrac{\alpha}{n}$$

(α=degree of association at the given concentration)

$$\therefore \text{Total particle after association} = 1-\alpha+\frac{\alpha}{n}$$

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

$$\boxed{\alpha_{\text{association}} = \frac{i-1}{\dfrac{1}{n}-1}} \quad or \quad \boxed{\alpha_{\text{association}} = \frac{1-i}{1-\dfrac{1}{n}}}$$