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basic concepts

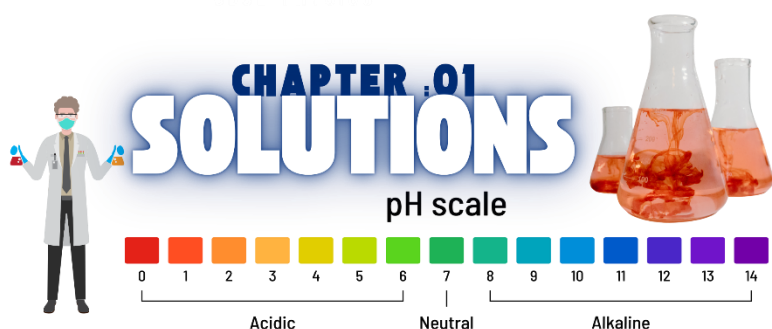
A solution is a mixture in which substances are intermixed so intimately that they cannot be observed as separate components. The dispersed phase or the substance which is to be dissolved is called solute, while the dispersion medium in which the solute is dispersed to get a homogenous mixture is called the solvent. And the Solubility of a substance may be defined as the amount of solute dissolved in 100gms of a solvent to form a saturated solution at a given temperature.

A saturated solution is a solution which contains at a given temperature as much solute as it can hold in presence of dissolving solvent. Any solution may contain less solute than would be necessary to saturate it. Such a solution is known as unsaturated solution. When the solution contains more solute than would be necessary to saturate it then it is termed as supersaturated solution.

Aqueous-solution reactions can lead to the formation of a solid, as when a solution of potassium chromate (K_2CrO_4) is added to an aqueous solution of barium nitrate $Ba(NO_3)_2$ to form solid barium chromate ($BaCrO_4$) and a solution of potassium nitrate (KNO_3). This reaction is described in the essay on Chemical Reactions.

We have primarily discussed liquid solutions, and in particular aqueous solutions. It should be stressed, however, that solutions can also exist in the gaseous or solid phases. The air we breathe is a solution, not a compound: in other words, there is no such thing as an “air molecule” Instead, it is made up of diatomic elements (those in which two atoms join to form a molecule of a single element); monatomic elements (those elements that exist as single atoms); one element in a tri-atomic molecule; and two compounds.

The “solvent” in air is nitrogen, a diatomic element that accounts for 78% of Earth's atmosphere. Oxygen, also diatomic, constitutes an additional 21%. Argon, which like all noble gases is monatomic, ranks a distant third, with 0.93%. The remaining 0.07% is made up of traces of other noble gases; the two compounds mentioned, carbon dioxide and water (in vapour form); and, high in the atmosphere, the tri-atomic form of oxygen known as ozone (O_3).



The most significant solid solutions are alloys of metals, discussed in the essay on Mixtures, as well as in essays on various metal families, particularly the Transition Metals. Some well-known alloys include bronze (three-quarters copper, one-quarter tin); brass (two-thirds copper, one-third zinc); pewter (a mixture of tin and copper with traces of antimony); and numerous alloys of iron—particularly steel—as well as alloys involving other metals.

Kinds of Solutions: All the three states of matter (gas, liquid or solid) may behave either as solvent or solute. Depending on the state of solute or solvent, mainly there may be following nine types of binary solutions. Among these solutions the most significant type of solutions are those which are in liquid phase and may be categorised as:

- Solid in liquid solutions,
- Liquid in liquid solutions
- Gas in liquid solutions.

Table 3.1: Solvent, Solute and Example

Solvent	Solute	Example
Gas	Gas	Mixture of gases, air.
Gas	Liquid	Water vapours in air, mist.
Gas	Solid	Sublimation of a solid into a gas, smoke.
Liquid	Gas	CO_2 gas dissolved in water (aerated drinks).
Liquid	Liquid	Mixture of miscible liquids, e.g., alcohol in water.
Liquid	Solid	Salt in water, sugar in water.
Solid	Gas	Adsorption of gases over metals; hydrogen over palladium.
Solid	Liquid	Mercury in zinc, mercury in gold, $CuSO_4 \cdot 5H_2O$
Solid	Solid	Homogeneous mixture of two or more metals (alloys), e.g., copper in gold, zinc in copper.

Water and oil are immiscible due to their respective molecule structures, and hence their inherent characteristics of intermolecular bonding. Water molecules are polar, meaning that the positive electric charge is at one end of the molecule, while the negative charge is at the other end. Oil, on the other hand, is non-polar—charges are more evenly distributed throughout the molecule. The immiscible quality of oil and water in relation to one another explains a number of phenomena from the everyday world.

The dispersion of two substances in an emulsion is achieved through the use of an emulsifier or surfactant. Made up of molecules that are both water- and oil-soluble, an emulsifier or

surfactant acts as an agent for joining other substances in an emulsion. The two words are virtually synonymous, but “emulsifier” is used typically in reference to foods, whereas “surfactant” most often refers to an ingredient in detergents and related products.

In an emulsion, millions of surfactants surround the dispersed droplets of solute, known as the internal phase, shielding them from the solvent or external phase. Surfactants themselves are often used in laundry or dish detergent, because most stains on plates or clothes are oil-based, whereas the detergent itself is applied to the clothes in a water-based external phase. The emulsifiers in milk help to bond oily particles of milk fat (cream) and protein to the external phase of water that comprises the majority of milk's volume.

Colligative Properties: Certain properties of dilute solutions containing non-volatile solute do not depend upon the nature of the solute dissolved but depend only upon the concentration *i.e.*, the number of particles of the solute present in the solution. Such properties are called colligative properties.

- Lowering of vapour pressure of the solvent.
- Osmotic pressure of the solution.
- Elevation in boiling point of the solvent.
- Depression in freezing point of the solvent.

Since colligative properties depend upon the number of solute particles present in the solution, the simple case will be that when the solute is a non-electrolyte. In case the solute is an electrolyte, it may split to a number of ions each of which acts as a particle and thus will affect the value of the colligative property. Each colligative property is exactly related to other; Relative lowering of vapour pressure, elevation in boiling point and depression in freezing point are directly proportional to osmotic pressure.

Vapour Pressure: The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called vapour pressure of the liquid. The vapour pressure of a liquid depends on:

- Nature of Liquid:** Liquids, which have weak intermolecular forces, are volatile and have greater vapour pressure. For example, dimethyl ether has greater vapour pressure than ethyl alcohol.
- Temperature:** Vapour pressure increases with increase in temperature. This is due to the reason that with increase in temperature more molecules of the liquid can go into vapour phase.

- Purity of liquid:** Pure liquid always has a vapour pressure greater than its solution.

Raoult's Law: When a non-volatile substance is dissolved in a liquid, the vapour pressure of the liquid (solvent) is lowered. According to Raoult's law (1887), at any given temperature the partial vapour pressure (p_A) of any component of a solution is equal to its mole fraction (X_A) multiplied by the vapour pressure of this component in the pure state (p_A°). That is, $p_A = p_A^\circ \times X_A$

The vapour pressure of the solution (P_{total}) is the sum of the partial pressures of the components, *i.e.*, for the solution of two volatile liquids with vapour pressures p_A and p_B .

$$P_{\text{total}} = p_A + p_B = (p_A^\circ \times X_A) + (p_B^\circ \times X_B)$$

Relative lowering of vapour pressure is defined as the ratio of lowering of vapour pressure to the vapour pressure of the pure solvent. It is determined by Ostwald-Walker method.

$$\text{Thus according to Raoult's law, } \frac{p^\circ - p}{p^\circ} = \frac{n}{n + N} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

Where, p = Vapour pressure of the solution

p° = Vapour pressure of the pure solvent

n = Number of moles of the solute

N = Number of moles of the solvent

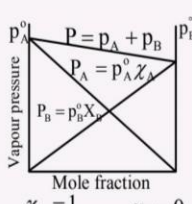
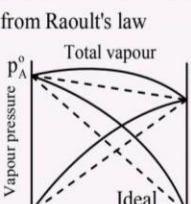
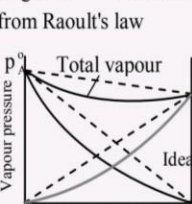
w and m = weight and mol. wt. of solute

W and M = weight and mol. wt. of the solvent.

Limitations of Raoult's Law

- Raoult's law is applicable only to very dilute solutions.
- Raoult's law is applicable to solutions containing non-volatile solute only.
- Raoult's law is not applicable to solutes which dissociate or associate in the particular solution.

Table 3.2: Ideal and Non-ideal Solutions

Ideal solutions	Non-ideal solutions	
 <p>Partial vapour pressure curves are straight lines. Total vapour pressure is a straight line connecting the pure component vapour pressures.</p> <p>$P = p_A + p_B$ $p_A = p_A^\circ X_A$ $p_B = p_B^\circ X_B$</p> <p>Mole fraction $X_A = 1$ $X_A = 0$ $X_B = 0$ $X_B = 1$</p>	<p>Positive deviation from Raoult's law</p>  <p>Partial vapour pressure curves are concave down. Total vapour pressure is a curve above the ideal line.</p> <p>Mole fraction $X_A = 1$ $X_B = 1$ $X_B = 0$ $X_A = 0$</p>	<p>Negative deviation from Raoult's law</p>  <p>Partial vapour pressure curves are concave up. Total vapour pressure is a curve below the ideal line.</p> <p>Mole fraction $X_A = 1$ $X_A = 0$ $X_B = 0$ $X_B = 1$</p>

Obey Raoult's law at every range of concentration.	Do not obey Raoult's law.	Do not obey Raoult's law.
$\Delta H_{\text{mix}} = 0$; neither heat is evolved nor absorbed during dissolution.	$\Delta H_{\text{mix}} > 0$. Endothermic dissolution; heat is absorbed.	$\Delta H_{\text{mix}} < 0$. Exothermic dissolution; heat is evolved.
$\Delta V_{\text{mix}} = 0$; total volume of solution is equal to sum of volumes of the components.	$\Delta V_{\text{mix}} > 0$. Volume is increased after dissolution.	$\Delta V_{\text{mix}} < 0$. Volume is decreased during dissolution.
$P = p_A + p_B$ $= p_A^\circ X_A + p_B^\circ X_B$ i.e., $p_A = p_A^\circ X_A : p_B$ $= p_B^\circ X_B$	$p_A > p_A^\circ X_A$ $p_B > p_B^\circ X_B$ $\therefore p_A + p_B > p_A^\circ X_A + p_B^\circ X_B$	$p_A < p_A^\circ X_A$ $p_B < p_B^\circ X_B$ $\therefore p_A + p_B < p_A^\circ X_A + p_B^\circ X_B$
A-A, A-B, B-B interactions should be same, i.e., 'A' and 'B' are identical in shape, size and character.	A-B attractive force should be weaker than A-A and B-B attractive forces. 'A' and 'B' have different shape, size and character.	A-B attractive force should be greater than A-A and B-B attractive forces. 'A' and 'B' have different shape, size and character.
Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.	'A' and 'B' escape easily showing higher vapour pressure than the expected value.	Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.
Examples: Dilute solutions; benzene + toluene; n-hexane + n-heptane; chlorobenzene + bromobenzene; ethyl bromide + ethyl iodide; n-butyl chloride + n-butyl bromide	Examples: Acetone + ethanol; acetone + CS_2 ; water + methanol; water + ethanol; CCl_4 + toluene; CCl_4 + CHCl_3 ; acetone + benzene; CCl_4 + CH_3OH ; cyclohexane + ethanol	Examples: Acetone + aniline; acetone + chloroform; CH_3OH + CH_3COOH ; H_2O + HNO_3 ; chloroform + diethyl ether; water + HCl ; acetic acid + pyridine; chloroform + benzene

Osmotic Pressure (π): The osmotic pressure is a colligative property. For a given solvent the osmotic pressure depends only upon the molar concentration of solute but does not depend upon its nature. The following relation relates osmotic pressure to the number of moles of the solute,

According to Boyle Van't

Hoff law (at conc. temp.) $\pi \propto C$. . . (i)

According to Gaylussac Van't

Hoff law (at conc. temp.) $\pi \propto T$. . . (ii)

From equation (i) and (ii) we get $\pi \propto CT$

$\pi = CRT$ (Van't Hoff equation)

$$\pi = \frac{n}{V} RT \quad \left(\because C = \frac{n}{V} \right);$$

$$\pi = \frac{w}{m} \frac{RT}{V} \quad \left(\because n = \frac{w}{m} \right)$$

Here, C = concentration of solution in moles per litre

R = gas constant

T = temperature

n = number of moles of solute

V = volume of solution

m = molecular weight of solute

w = weight of solute

Relation of Osmotic Pressure with Different Colligative

Properties: Osmotic pressure is related to relative lowering of vapour pressure, elevation of boiling point and depression of freezing point according to the following relations,

$$(a) \pi = \left(\frac{P_A^\circ - P_A}{P_A^\circ} \right) \times \frac{dRT}{M}$$

$$(b) \pi = \Delta T_b \times \frac{dRT}{1000 \times K_b}$$

$$(c) \pi = \Delta T_f \times \frac{dRT}{1000 \times K_f}$$

In the above relations,

π = Osmotic pressure

d = Density of solution at temperature T

R = Universal gas constant

M = Mol. Mass of solute

K_b = Molal elevation constant of solvent

K_f = Molal depression constant of solvent

Isotonic, Hypertonic and Hypotonic Solutions

- Isotonic or iso-osmotic solutions:** Two solutions of different substances having same osmotic pressure at same temperature are known as isotonic solutions.

For isotonic solutions, $\pi_1 = \pi_2$ Primary Condition . . . (i)

Also, $C_1 = C_2$

$$\left. \begin{array}{l} \text{or } \frac{n_1}{V_1} = \frac{n_2}{V_2} \\ \text{or } \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2} \end{array} \right\} \text{Secondary Conditions} \quad \dots (ii)$$

Equation (ii) holds good only for those solutes which neither possess the tendency to get associate nor dissociate in solution, e.g.,

Urea and glucose are isotonic then, $\pi_1 = \pi_2$ and $C_1 = C_2$

Urea and NaCl are isotonic then, $\pi_1 = \pi_2$ but $C_1 \neq C_2$
(dissociate)

Urea and Benzoic acid are isotonic then, $\pi_1 = \pi_2$ but $C_1 \neq C_2$
(associate)

- **Hypertonic and hypotonic solution:** The solution which has more osmotic pressure than the other solution is called as hypertonic solution and the solution which has lesser osmotic pressure than the other is called as hypotonic solution. The flow of solvent is always from lower osmotic pressure to higher osmotic pressure i.e. from hypotonic to hypertonic solution.

Ebullioscopy: Elevation in boiling point is determined by Landsberger's method and Cottrell's method. Study of elevation in boiling point of a liquid in which a non-volatile solute is dissolved is called as ebullioscopy.

Boiling point of a liquid may be defined as the temperature at which its vapour pressure becomes equal to atmospheric pressure, i.e., 760 mm. Since the addition of a non-volatile solute lowers the vapour pressure of the solvent, solution always has lower vapour pressure than the solvent and hence it must be heated to a higher temperature to make its vapour pressure equal to atmospheric pressure with the result the solution boils at a higher temperature than the pure solvent. Thus sea water boils at a higher temperature than distilled water. If T_b is the boiling point of the solvent and T is the boiling point of the solution, the difference in the boiling point (ΔT or ΔT_b) is called the elevation of boiling point.

$$T - T_b = \Delta T_b \text{ or } \Delta T$$

Important Relations Concerning Elevation in Boiling Point

- The elevation of boiling point is directly proportional to the lowering of vapour pressure, i.e., $\Delta T_b \propto p^0 - p$

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

Where K_b = molal elevation constant or ebullioscopic constant of the solvent; m = Molality of the solution, i.e., number of moles of solute per 1000g of the solvent; ΔT_b = Elevation in boiling point

$$\Delta T_b = \frac{1000 \times K_b \times w}{m \times W} \text{ or } m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

where, K_b is molal elevation constant and defined as the elevation in b.pt. produced when 1 mole of the solute is dissolved in 1 kg of the solvent. w and W are the weights of solute and solvent and m is the molecular weight of the solute.

$$K_b = \frac{0.002(T_0)^2}{l_v}$$

where T_0 = Normal boiling point of the pure solvent; l_v = Latent heat of evaporation in cal/g of pure solvent; K_b for water is $0.52 \text{ deg} - \text{kg mol}^{-1}$.

Cryoscopy: Depression in freezing point is determined by Beckmann's method and Rast's camphor method. Study of depression in freezing point of a liquid in which a non-volatile solute is dissolved in it is called as cryoscopy.

Freezing point is the temperature at which the liquid and the solid states of a substance are in equilibrium with each other or it may be defined as the temperature at which the liquid and the solid states of a substance have the same vapour pressure. It is observed that the freezing point of a solution is always less than the freezing point of the pure solvent. Thus the freezing point of sea water is low than that of pure water. The depression in freezing point (ΔT or ΔT_f) of a solvent is the difference in the freezing point of the pure solvent (T_s) and the solution (T_{sol}).

$$T_s - T_{sol} = \Delta T_f \text{ or } \Delta T$$

NaCl or CaCl_2 (anhydrous) are used to clear snow on roads. They depress the freezing point of water and thus reduce the temperature of the formation of ice.

Important Relations Concerning Depression in Freezing Point

- Depression in freezing point is directly proportional to the lowering of vapour pressure. $\Delta T_f \propto p^0 - p$
- $\Delta T_f = K_f \times m$ where K_f = molal depression constant or cryoscopic constant; m = Molality of the solution (i.e., no. of moles of solute per 1000g of the solvent); ΔT_f = Depression in freezing point

$$\Delta T_f = \frac{1000 \times K_f \times w}{m \times W} \text{ or } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Where K_f is molal depression constant and defined as the depression in freezing point produced when 1 mole of the solute is dissolved in 1 kg of the solvent. w and W are the weights of solute and solvent and m is the molecular weight of the solute.

$$K_f = \frac{R(T_0)^2}{l_f 1000} = \frac{0.002(T_0)^2}{l_f}$$

Where T_0 = Normal freezing point of the solvent; l_f = Latent heat of fusion/g of solvent; K_f for water is $1.86 \text{ deg} - \text{kg mol}^{-1}$

Colligative Properties of Electrolytes: The colligative properties of solutions, viz. lowering of vapour pressure, osmotic pressure, elevation in b.p. and depression in freezing point, depend on the total number of solute particles present in solution. Since the electrolytes ionise and give more than one particle per formula unit in solution, the colligative effect of an electrolyte solution is always greater than that of a non-

electrolyte of the same molar concentration. All colligative properties are used for calculating molecular masses of non-volatile solutes. However osmotic pressure is the best colligative property for determining molecular mass of a non-volatile substance.

Van't Hoff's Factor (*i*): In 1886, Van't Hoff introduced a factor '*i*' called Van't Hoff's factor, to express the extent of association or dissociation of solutes in solution. It is ratio of the normal and observed molecular masses of the solute, *i.e.*,

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

In case of association, observed molecular mass being more than the normal, the factor *i* has a value less than 1. But in case of dissociation, the Van't Hoff's factor is more than 1 because the observed molecular mass has a lesser value than the normal molecular mass. In case there is no dissociation the value of '*i*' becomes equal to one.

Since, colligative properties are inversely proportional to molecular masses, the Van't Hoff's factor may also be written as,

$$i = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligative property assuming no association or dissociation}}$$

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

Introduction of the Van't Hoff factor modifies the equations for the colligative properties as follows,

$$\text{Relative lowering of vapour pressure} = \frac{P_A^0 - P_A}{P_A^0} = iX_B$$

$$\text{Elevation of boiling point, } \Delta T_b = ik_b m$$

$$\text{Depression in freezing point, } \Delta T_f = ik_f m$$

$$\text{Osmotic pressure, } \pi = \frac{i n R T}{V}; \pi = i C R T$$

From the value of '*i*', it is possible to calculate degree of dissociation or degree of association of substance.

Degree of Dissociation(α)

It is defined as the fraction of total molecules which dissociate into simpler molecules or ions.

$$\alpha = \frac{i-1}{m-1} \quad m = \text{number of particles in solution}$$

Degree of Association (α): It is defined as the fraction of the total number of molecules which associate or combine together resulting in the formation of a bigger molecules.

$$\alpha = \frac{i-1}{1/m-1}; m = \text{number of particles in solution.}$$

Note

All colligative properties are used for calculating molecular masses of non-volatile solutes. However osmotic pressure is the best colligative property for determining molecular mass of a non-volatile substance.

(i) In case of non-electrolyte (glucose, sugar, urea etc), the value of colligative property depends directly on the concentration. If the substance is an electrolyte [NaCl, BaCl₂ etc], its dissociation to colligative property depends upon concentration of ions [*e.g.* – 0.1 M NaCl = 0.2 M ions, 0.1 M BaCl₂ = 0.3 M ions].

(ii) $i_{(\text{Na}_3\text{PO}_4)} \longrightarrow$ Highest (It gives max. ions)

(iii) $i_{(\text{association})} < i_{(\text{dissociation})}$

(iv) For 0.1 M solution, the colligative property will follow the order NaCl < Na₂SO₄ < Na₃PO₄.

(v) 1 M has higher concentration than 1 m (aq. Solution).

(vi) Mole fraction of any component in the vapour phase

$$= \frac{\text{Partial V.P. of that component}}{\text{Total vapour pressure}}$$

$$(vii) D = \frac{M}{V}$$

(viii) Ethylene glycol (anti freeze) lowers the F. Pt.

(ix) $\alpha = 1$ [For 100% dissociation of solute]

(x) Camphor has the maximum value of K_f (39.7°) (Maximum F. P. falls in camphor).

(xi) For water, $K_b = 0.52^\circ$; $K_f = 1.86^\circ$

(xii) K_f and K_b not colligative property.

(xiii) Relationship between different colligative properties

$$\pi \text{ with relative lowering of V. P. ; } \pi = \frac{P_A^0 - P_A}{P_A^0} \times \frac{d R T}{M_B};$$

where *d* = density of the solution at temperature *T*

$$\pi \text{ with } \Delta T_b; \pi = \Delta T_b \times \frac{d R T}{1000 K_b}$$

$$\pi \text{ with } \Delta T_f; \pi = \Delta T_f \times \frac{d R T}{1000 K_f}$$

ΔT_b with relative lowering of V. P. ;

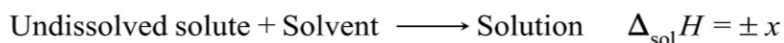
$$\Delta T_b = \frac{1000 K_b}{M_A} \left(\frac{P_A^0 - P_A}{P_A^0} \right)$$

$$\Delta T_f = \frac{1000 k_f}{M_A} \left(\frac{P_A^0 - P_A}{P_A^0} \right)$$

(xiv) Plasmolysis: When a plant cell is placed in a hyper tonic solution, the fluid from the plant cell comes out and cell shrinks. This phenomenon is called plasmolysis and is due to osmosis.

Causes of solubility: The following types of forces of attraction are operated when a solute is mixed with a solvent:

- (i) **Inter-ionic attraction in the solute molecules:** Ions are held together in the lattice due to electrostatic forces. Due to these forces molecules are stabilised and the energy released is called **lattice energy**. This is defined as the energy released when 1 g mole of the compound is formed due to electrostatic attraction between the ions.
- (ii) **Inter-molecular attraction between solvent molecules:** Water is a **polar solvent** because of the difference in electronegativity between hydrogen and oxygen atoms constituting water molecule. This difference gives rise to the development of a slight negative charge on oxygen and equal positive charge on hydrogen. A dipole is thus created giving rise to dipole-dipole attraction between water molecules.
- (iii) **Solvation:** It represents force of attraction between solute and solvent molecules. If the solvent is water then the energy released is called **hydration energy**.
If hydration energy > lattice energy, then solution is easily formed. Both the ions of the solute get hydrated to overcome the lattice energy of the solute.
- (iv) **Temperature:** Saturated solution represents equilibrium between undissolved solute and dissolved solute.



If $\Delta_{\text{sol}} H < 0$, i.e., (–ve), the dissolution is exothermic. In this case, as the temperature increases, solubility decreases (Le Chatelier's principle).

If $\Delta_{\text{sol}} H > 0$, i.e., (+ve), there is endothermic dissolution. In this case, increase in temperature increases the solubility (Le Chatelier's principle).

(b) **Liquid-liquid solutions:** When two liquids are mixed, three different situations result:

- (i) **Miscible liquids:** The two components are completely soluble. They are miscible only when they have similar nature or belong to the same homologous series. Example: water and alcohol (both polar), benzene-toluene (both belong to the same homologous series). There is a rule:

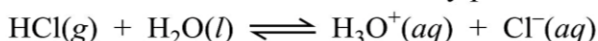
Like dissolves like – Polar solute is soluble in polar solvent and a non-polar one in a non-polar solvent.

- (ii) **Partially miscible liquids:** This happens only when the intermolecular forces of one liquid is greater than that of the other is. Solubility, however, increases with increasing temperature. Examples: aniline-water, phenol-water.

- (iii) **Immiscible liquids:** Two components are completely immiscible. This happens when one liquid is polar and the other is non-polar. Examples: Carbon tetrachloride-water; chloroform-water.

(c) **Gas-liquid solutions:** The gases are generally soluble in water and to a limited extent in other solvents too. Solubility, however, depends on the following factors:

- (i) **Nature of gas:** Easily liquefiable gases are generally more soluble in common solvents.
- (ii) **Nature of liquid:** Those gases which easily form ions in solution are more soluble in water than in other solvents. Ion formation in other solvents is not an easy process.



- (iii) **Pressure:** Pressure is an important factor affecting the solubility of gas in liquids. This is governed by Henry's law.

- (iv) **Temperature:** With rise in temperature, the solubility generally decreases because gas is expelled. Some gases, however, find their solubility increased at a higher temperature.

➔ **Henry's law:** It states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas.

The most commonly used form of Henry's law states that the partial pressure (p) of a gas in vapour phase 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 and x is the mole fraction of the gas.

Note: Mole fraction is discussed in detail further in this chapter.

Limitations of Henry's Law:

Henry's law is applicable only when

- The pressure of the gas is not too high and temperature is not too low.
- The gas should not undergo any chemical change.
- The gas should not undergo association or dissociation in the solution.

Applications of Henry's Law:

- To increase the solubility of CO_2 in soda water and soft drinks, the bottle is sealed under high pressure.
- To avoid the toxic effects of high concentration of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- At high altitudes, low blood oxygen causes climbers to become weak and make them unable to think clearly, which are symptoms of a condition known as anoxia.

3. Methods of Expressing Concentration of Solutions:

The concentration of solution is the amount of the solute present in the given quantity of solution or solvent. It can be expressed in any of the following ways:

(a) Mass percentage (w/w): It may be defined as mass of solute per 100 g of solution.

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

(b) Volume percentage (V/V): It may be defined as volume of solute per 100 mL of solution.

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

(c) Mass by volume percentage (w/V): It may be defined as the mass of solute per 100 mL of the solution.

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

(d) Parts per million (ppm): It is the parts of a component per million (10^6) parts of the solution.

$$\text{ppm} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

It is convenient to express concentration in ppm when a solute is present in trace quantities.

(e) Mole fraction (x): It may be defined as the ratio of the number of moles of one component (solute or solvent) to the total number of moles of all the components present in the solution.

If in a solution, n_A and n_B are the number of moles of solvent and solute, respectively, then

Mole fraction of solvent in the solution,

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

Mole fraction of solute in the solution,

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

In a solution, sum of the mole fractions of all the components is unity. For example, in a binary solution (having two components), $x_A + x_B = 1$.

(f) Molarity (M): It is defined as number of moles of solute dissolved in one litre of solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in litre)}}$$

Unit of molarity is mol L^{-1} or M (molar). Molarity changes with change in temperature as volume changes with change in temperature.

(g) Molality (*m*): It is defined as the number of moles of the solute dissolved in one kilogram (kg) of the solvent and is expressed as:

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent (in grams)}} \times 1000$$

Unit of molality is mol kg^{-1} or molal (*m*).

Molality is independent of temperature.

4. Vapour Pressure of Pure Liquid and Solution

Vapour pressure: When a liquid is taken in a closed vessel, a part of the liquid evaporates and its vapours occupy the available empty space. These vapours cannot escape as the vessel is closed. They would rather have a tendency to condense into liquid form. In fact an equilibrium is established between vapour phase and liquid phase and the pressure that its vapour exerts is termed as vapour pressure. Thus, vapour pressure of a liquid may be defined as the pressure exerted by the vapours above the liquid surface in equilibrium with the liquid phase at a given temperature.

The vapour pressure of a liquid depends on the following factors:

Nature of the liquid: Liquids having weak intermolecular forces are volatile and therefore have greater vapour pressure.

Temperature: Vapour pressure of a liquid increases with increase in temperature. This is because with increase in temperature, the kinetic energy of the molecules increases and therefore large number of molecules are available for escaping from the surface of the liquid.

(a) Vapour pressure of liquid–liquid solution:

Raoult's Law for solutions of volatile liquids: It states that for a solution of volatile liquids the partial pressure of each component of the solution is directly proportional to its mole fraction present in a solution. Mathematically,

$$\begin{aligned} p_A &\propto x_A & p_B &\propto x_B \\ p_A &= p_A^\circ x_A & p_B &= p_B^\circ x_B \end{aligned}$$

where p_A and p_B are partial vapour pressures, x_A and x_B are mole fractions, p_A° and p_B° are the vapour pressure of pure components *A* and *B* respectively.

If p is total vapour pressure then according to Dalton's law of partial pressure,

$$\begin{aligned} p &= p_A + p_B \\ &= p_A^\circ x_A + p_B^\circ x_B \\ &= p_A^\circ (1 - x_B) + p_B^\circ x_B \\ &= p_A^\circ + (p_B^\circ - p_A^\circ) x_B \end{aligned}$$

As p_A° and p_B° are constants at a given temperature, it is evident from the above equations that the total vapour pressure varies linearly with the mole fraction x_B (or x_A since $x_A = 1 - x_B$).

The composition of the vapour phase in equilibrium with the solution can be determined from the partial pressure of the two components. If y_A and y_B are the mole fractions of components *A* and *B* respectively in the vapour phase, then

$$\begin{aligned} p_A &= y_A p_{\text{total}} \\ p_B &= y_B p_{\text{total}} \end{aligned}$$

In general,

$$p_i = y_i p_{\text{total}}$$

➔ Raoult's law as a special case of Henry's law.

In the solution of a gas in a liquid, if one of the components is so volatile that it exists as a gas, then it can be said that Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_A° .

(b) Vapour pressure of solutions of solids in liquids

Raoult's law for a solution containing a non-volatile solute and volatile solvent: It states that the relative lowering of vapour pressure is equal to mole fractions of solute which is non-volatile.

Mathematically,

$$p = p_A + p_B$$

or,

$$p = p_A \text{ (Since solute } B \text{ is non-volatile)}$$

$$p = p_A^\circ x_A$$

$$p = p_A^0 (1 - x_B) = p_A^0 - p_A^0 x_B$$

$$p_A^0 x_B = p_A^0 - p$$

$$\frac{p_A^0 - p}{p_A^0} = x_B$$

or

or Relative lowering of vapour pressure = Mole fraction of solute

5. Ideal and Non-Ideal Solutions

(a) Ideal solution: A solution is called an ideal solution if it obeys Raoult's law over a wide range of concentration (Fig. 2.1) at a specified temperature.

For an ideal solution,

$$p = p_A + p_B = p_A^0 x_A + p_B^0 x_B$$

Liquids having similar nature and structure are likely to form ideal solutions. Examples are:

- Mixture of methanol and ethanol
- Mixture of *n*-hexane and *n*-heptane
- Mixture of benzene and toluene.

Reasons for formation of ideal solutions: A solution of two miscible liquids *A* and *B* will be ideal if two essential conditions are fulfilled.

(i) If F_{A-A} is the force of attraction between molecules of *A* and F_{B-B} is that of molecules of *B*, then *A* and *B* will form an ideal solution only if,

$$F_{A-B} = F_{A-A} = F_{B-B}$$

(ii) The solution of *A* and *B* liquids will be ideal if *A* and *B* have similar structures and polarity. Methanol and ethanol have the same functional group and almost same polarity and therefore, form ideal solutions.

For an ideal solution

(i) Raoult's law is obeyed, i.e., $p_A = p_A^0 x_A$ and $p_B = p_B^0 x_B$

(ii) $\Delta_{\text{mix}} H = 0$ and

(iii) $\Delta_{\text{mix}} V = 0$.

(b) Non-ideal solution: A solution which does not obey Raoult's law for all concentrations is called a non-ideal solution.

For a non-ideal solution

(i) Raoult's law is not obeyed,

$$\text{i.e., } p_A \neq p_A^0 x_A \text{ and } p_B \neq p_B^0 x_B$$

(ii) $\Delta_{\text{mix}} H \neq 0$ and

(iii) $\Delta_{\text{mix}} V \neq 0$.

A non-ideal solution can show either positive or negative deviation from Raoult's law.

(A) Positive Deviation: The deviation will be called positive when the partial pressure of each component and the resultant total pressure are greater than the pressure expected on the basis of Raoult's law (Fig. 2.2).

In such cases, the intermolecular forces between solvent-solute molecules (F_{A-B}) are weaker than those between solvent-solvent (F_{A-A}) and solute-solute (F_{B-B}) molecules. That is,

$$F_{A-B} < F_{A-A} \text{ and } F_{B-B}$$

This shows that the molecules of *A* or *B* will escape more easily from the surface of the solution, i.e., the vapour pressure of solution will be higher.

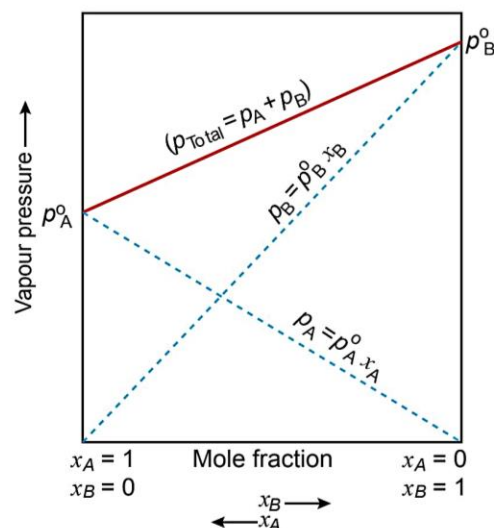


Fig. 2.1: Vapour pressure diagram for an ideal solution

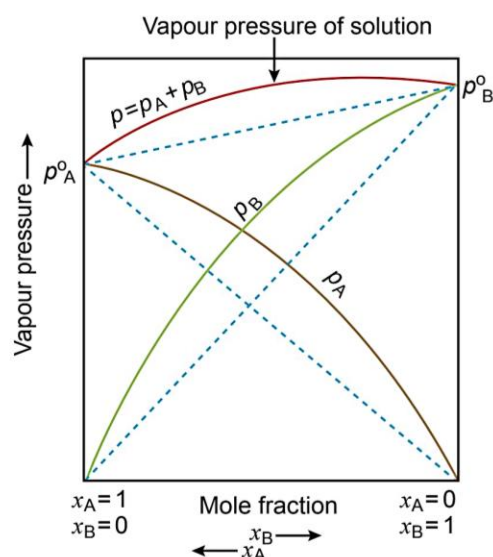


Fig. 2.2: Vapour pressure diagram showing positive deviation

Characteristics of a Solution Showing Positive Deviation

- $p_A > p_A^0 x_A$; $p_B > p_B^0 x_B$
- $\Delta_{\text{mix}} H > 0$, i.e., +ve,
- $\Delta_{\text{mix}} V > 0$, i.e., +ve,

Some examples of the solution exhibiting positive deviations are:

- Ethyl alcohol and water
- Acetone and carbon disulphide
- Carbon tetrachloride and benzene
- Acetone and benzene

(B) Negative Deviation: The deviation is called negative deviation, if the partial pressure of each component (A and B) and resultant total vapour pressure are less than the pressure expected on the basis of Raoult's law. (Fig. 2.3)

This type of deviation is shown by the solutions in which

$$F_{A-B} > F_{A-A} \quad \text{and} \quad F_{B-B}$$

Due to this, there is decrease in the escaping tendency of A or B molecules from the surface of solution.

Consequently, the vapour pressure of the solution will be lower.

Characteristics of a Solution Showing Negative Deviation

- $p_A < p_A^0 x_A$; $p_B < p_B^0 x_B$
- $\Delta_{\text{mix}} H < 0$, i.e., -ve, because weak $A-A$ and $B-B$ bonds are broken and strong $A-B$ bond is formed. Heat is consequently released.
- $\Delta_{\text{mix}} V < 0$, i.e., -ve,

Some examples of the solution showing negative deviations are

- HNO_3 and water
- Chloroform and acetone
- Acetic acid and pyridine
- Hydrochloric acid and water

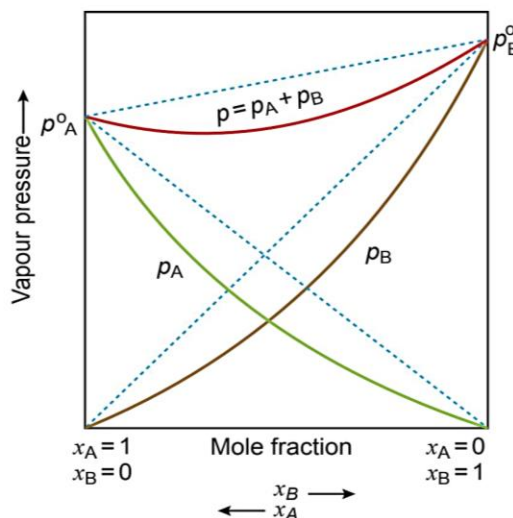


Fig. 2.3: Vapour pressure diagram showing negative deviation

Table 2.2: Characteristics of Ideal and Non-ideal Solutions

S.No.	Ideal Solutions	Non-ideal Solutions	
		Positive Deviation	Negative Deviation
(i)	$F_{A-A} = F_{B-B} = F_{A-B}$	$F_{A-B} < F_{A-A}$ and F_{B-B}	$F_{A-B} > F_{A-A}$ and F_{B-B}
(ii)	$p_A = p_A^0 x_A$; $p_B = p_B^0 x_B$	$p_A > p_A^0 x_A$; $p_B > p_B^0 x_B$	$p_A < p_A^0 x_A$; $p_B < p_B^0 x_B$
(iii)	$\Delta_{\text{mix}} H = 0$	$\Delta_{\text{mix}} H > 0$, i.e., +ve	$\Delta_{\text{mix}} H < 0$, i.e., -ve
(iv)	$\Delta_{\text{mix}} V = 0$	$\Delta_{\text{mix}} V > 0$, i.e., +ve	$\Delta_{\text{mix}} V < 0$, i.e., -ve

Azeotropes or Azeotropic mixture: Azeotropes are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.

Types of Azeotropes:

- Minimum boiling azeotropes:** These are the binary mixtures whose boiling point is less than either of the two components. The non-ideal solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition, e.g., a mixture of 94.5% ethyl alcohol and 4.5% water by volume.

(ii) **Maximum boiling azeotropes:** These are the binary mixtures whose boiling point is more than either of the two components. The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition, e.g., a mixture of 68% HNO_3 and 32% H_2O by mass.

6. Colligative Properties

Those properties which depend on the number of solute particles (molecules, atoms or ions) but not upon their nature are called colligative properties. The following are the colligative properties:

- Relative lowering of vapour pressure of the solvent,
- Elevation of boiling point of the solvent,
- Depression of freezing point of the solvent,
- Osmotic pressure of the solution.

(a) **Relative lowering of vapour pressure:** The addition of a non-volatile solute to a volatile solvent decreases the escaping tendency of the solvent molecules from the surface of solutions as some of the surface area is occupied by non-volatile solute particles. According to Raoult's law, the relative lowering of vapour pressure is equal to mole fraction of solute.

Thus,

$$\frac{p_A^o - p}{p_A^o} = x_B = \frac{n_B}{n_A + n_B}$$

For a dilute solution, $n_B \ll n_A$, hence neglecting n_B in the denominator, we have

$$\frac{p_A^o - p}{p_A^o} = \frac{n_B}{n_A} = \frac{W_B \times M_A}{M_B \times W_A}$$

$$M_B = \left(\frac{p_A^o}{p_A^o - p} \right) \times \frac{W_B \times M_A}{W_A}$$

(b) **Elevation of boiling point:** Boiling point is the temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure. When a non-volatile solute is added to a volatile solvent, the vapour pressure of the solvent decreases. In order to make this solution boil, its vapour pressure must be increased by raising the temperature above the boiling point of the pure solvent. The difference in the boiling point of solution (T_b^o) and that of pure solvent (T_b) is called elevation of boiling point (ΔT_b). Thus,

Elevation of boiling point = $\Delta T_b = T_b^o - T_b$
(Fig. 2.4)

For dilute solution, it has been found that the elevation of boiling point is directly proportional to the molal concentration of the solute in the solution. Thus,

$$\Delta T_b \propto m \text{ or } \Delta T_b = K_b m$$

where K_b is a constant called molal elevation constant or ebullioscopic constant.

When $m = 1 \text{ mol kg}^{-1}$, $\Delta T_b = K_b$

Hence, molal elevation constant may be defined as the elevation in boiling point when one mole of a non-volatile solute is dissolved in one kilogram (1000 g) of solvent. The unit of K_b is K kg mol^{-1} .

As

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

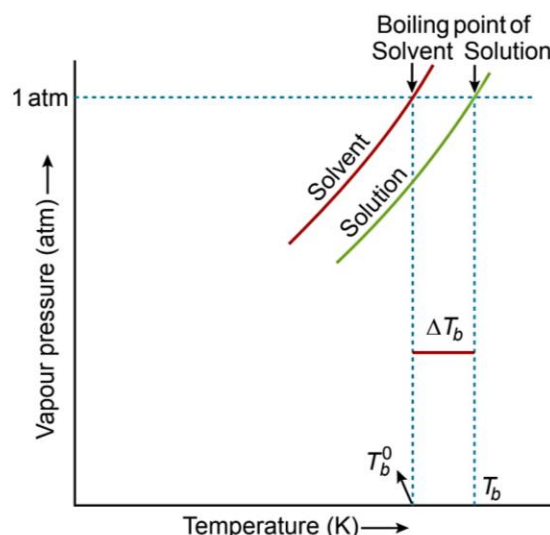


Fig. 2.4: Vapour pressure temperature curves showing elevation in boiling point of solution

Therefore,

$$\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A}$$

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

(c) Depression of freezing point: Freezing point is defined as the temperature at which the vapour pressure of a substance in its liquid phase is equal to its vapour pressure in the solid phase. A solution freezes when its vapour pressure equals the vapour pressure of the pure solid solvent. Whenever a non-volatile solute is added to the volatile solvent, its vapour pressure decreases and it would become equal to that of solid solvent at a lower temperature. The difference in the freezing point of pure solvent (T_f°) and that of the solution (T_f) is known as depression of freezing point (ΔT_f). Thus,

$$\text{Depression of freezing point} = \Delta T_f = T_f^\circ - T_f$$

It has been found that for a dilute solution, depression in freezing is directly proportional to molality of the solution.

$$\Delta T_f \propto m \text{ or } \Delta T_f = K_f m$$

where K_f is a constant called molal depression constant or cryoscopic constant.

$$\text{When } m = 1 \text{ mol kg}^{-1}, \quad \Delta T_f = K_f$$

Hence, molal depression constant may be defined as the depression in freezing point when one mole of non-volatile solute is dissolved in one kilogram (1000 g) of solvent. The unit of K_f is K kg mol^{-1} .

$$\text{Since, } m = \frac{W_B \times 1000}{M_B \times W_A}$$

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

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

The values of K_b and K_f which depend upon the nature of the solvent and concentration of the solution, can be ascertained from the following relations:

$$K_b = \frac{R \times M_A \times (T_b^\circ)^2}{\Delta_{\text{vap}} H \times 1000}$$

$$K_f = \frac{R \times M_A \times (T_f^\circ)^2}{\Delta_{\text{fus}} H \times 1000}$$

where,

R = Universal gas constant

M_A = Molecular mass of solvent

T_b° = Boiling point of pure solvent

$\Delta_{\text{vap}} H$ = Enthalpy of vapourisation of solvent

T_f° = Freezing point of pure solvent

$\Delta_{\text{fus}} H$ = Enthalpy of fusion of solid solvent

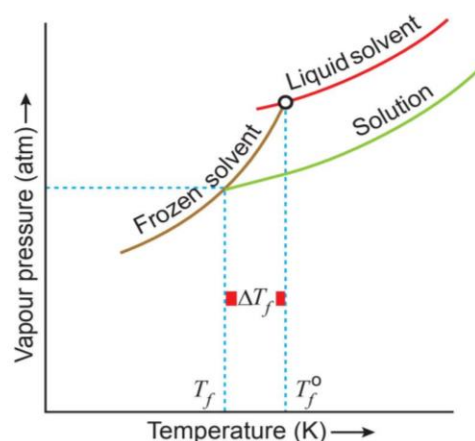


Fig. 2.5: Vapour pressure temperature curves showing depression in freezing point of solution

(d) **Osmosis:** When a solution is separated from its solvent by a semipermeable membrane (SPM) there is a spontaneous flow of solvent molecules from solvent compartment to solution compartment. The phenomenon is called osmosis. This movement of solvent is only in one direction. In diffusion, however, movement takes place in both the directions.

➔ **Semipermeable membrane (SPM):** A membrane through which only solvent molecules can pass but not the solute ones. Cellophane, parchment paper and the wall of living cell are the examples of SPM. It is also made of inorganic material, copper ferrocyanide $[\text{Cu}_2[\text{Fe}(\text{CN})_6]]$.

➔ **Osmotic pressure (π):** The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e., to stop the passage of solvent molecules into it through semipermeable membrane (Fig. 2.6).

Osmotic pressure (π) is proportional to molarity (C) of the solution at a given temperature T . Thus,

$$\pi = CRT$$

$$\text{or, } \pi = \frac{n_B}{V} RT = \frac{W_B \times R \times T}{M_B \times V}$$

$$\text{or, } M_B = \frac{W_B \times R \times T}{\pi \times V}$$

➔ **Reverse osmosis:** If a pressure larger than the osmotic pressure is applied to the solution side, the pure solvent (or water) flows out of the solution through the semipermeable membrane. In this way the direction of osmosis is reversed and so the process is called reverse osmosis (Fig. 2.7).

Thus, we can say that reverse osmosis is just opposite to the osmosis when an extra pressure is applied. Reverse osmosis is used in desalination to get pure water from sea water.

➔ **Isotonic solutions:** Two solutions are said to be isotonic when they exert the same osmotic pressure because they have the same molar concentration. All intravenous injections must be isotonic with body fluids.

➔ **Isosmotic solutions:** When two isotonic solutions are separated by a semipermeable membrane, no osmosis occurs. The solutions are called **isosmotic solutions**.

➔ **Hypotonic solutions:** A solution having lower osmotic pressure than the other solution is said to be hypotonic with respect to the other solution.

➔ **Hypertonic solution:** A solution having higher osmotic pressure than the other solution is said to be hypertonic with respect to other solution.

➔ **Plasmolysis:** When the cell is placed in a hypertonic solution, the fluid comes out of the cell due to osmosis and as a result cell material shrinks gradually. This process is called *plasmolysis*.

7. Abnormal Molar Masses

➔ **Association:** Association of molecules leads to decrease in the number of particles in the solution resulting in a decrease in the value of colligative property. As colligative property is inversely related to the molecular mass. Therefore, higher value is obtained for molecular mass than normal values.

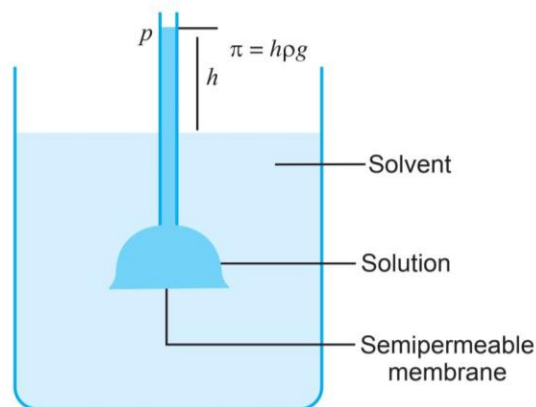


Fig. 2.6: The principle of measuring osmotic pressure: The pressure in excess of atmospheric pressure that must be applied to the solution to prevent it from rising in the tube is the osmotic pressure. This will also be equal to hydrostatic pressure of the liquid column of height, h .

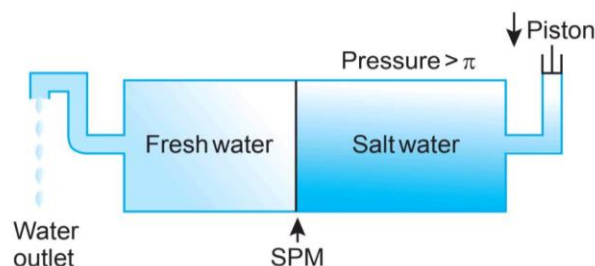
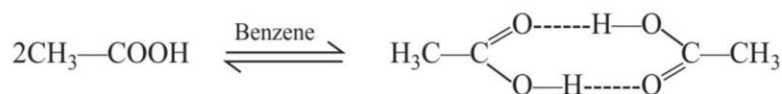
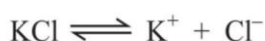


Fig. 2.7: Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution

For example, when ethanoic acid is dissolved in benzene it undergoes dimerisation and shows a molecular mass of 120 (normal molecular mass is 60).



- ➔ **Dissociation:** Dissociation leads to increase in the number of solute particles in the solution resulting in an increase in the value of colligative property. Since colligative property is inversely related to the molecular mass, therefore, molecular mass of such a substance as calculated from colligative property will be less than its normal value. For example, KCl is an electrolyte. When it is dissolved in water it dissociates into K^+ and Cl^- ions and there would be double the number of particles if complete dissociation takes place. Hence, it is expected to have molecular mass 37.25 g or $\left(\frac{74.5}{2}\right)$ g.



- ➔ **van't Hoff Factor (i):** It may be defined as the ratio of normal molecular mass to the observed molecular mass of the solute.

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

or,
$$i = \frac{\text{Observed colligative property}}{\text{Calculated value of colligative property}}$$

or,
$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of particles before association/dissociation}}$$

van't Hoff factor (i) expresses the extent of association or dissociation of the solute particles in the solutions.

In case of association, $i < 1$

In case of dissociation, $i > 1$

When there is neither association nor dissociation, $i = 1$

8. Modified Form of Colligative Properties

Inclusion of ' i ' modifies the equation for colligative properties as follows:

- ➔ Relative lowering of vapour pressure of solvent

$$\frac{p_A^o - p_A}{p_A^o} = i \frac{n_B}{n_A}$$

- ➔ Elevation of boiling point, $\Delta T_b = i K_b m$
 ➔ Depression of freezing point, $\Delta T_f = i K_f m$
 ➔ Osmotic pressure, $\pi = i CRT$

Important Formulae

In the formulae given below, A represents solvent and B represents solute, also

M_A = Molar mass of solvent

M_B = Molar mass of solute

W_A = Mass of solvent

W_B = Mass of solute

V = Volume of solution

d = Density of solution

GEM = Gram Equivalent Mass

GMM = Gram Molecular Mass

$$1. \text{ Mass percentage (w/w)} = \frac{W_B}{W_A + W_B} \times 100$$

$$\text{Volume percentage (V/V)} = \frac{V_B}{V_A + V_B} \times 100$$

$$\text{Mass by volume percentage } \left(\frac{w}{V} \right) = \frac{W_B \times 100}{V \text{ (mL)}}$$

$$\text{Parts per million (ppm)} = \frac{W_B}{W_A + W_B} \times 10^6$$

$$2. \text{ Mole fraction of A, } x_A = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of B, } x_B = \frac{n_B}{n_A + n_B}$$

$$x_A + x_B = 1$$

$$3. \text{ Molarity (M)} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}} = \frac{n_B}{V \text{ (in L)}} = \frac{W_B}{M_B \times V \text{ (in L)}}$$

$$4. \text{ Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \frac{n_B}{W_A \text{ (in kg)}} \text{ or } m = \frac{W_B \times 1000}{M_B \times W_A \text{ (in g)}}$$

$$5. \text{ Normality (N)} = \frac{\text{Gram equivalents of solute}}{\text{Volume of solution in litre}} = \frac{W_B}{\text{GEM of solute} \times V \text{ (in L)}}$$

6. Relationship between Molarity and Normality

The normality (N) and molarity (M) of a solution are related as follows:

$$\text{Normality} \times \text{Equivalent mass (solute)} = \text{Molarity} \times \text{Molar mass (solute)}$$

7. Relationship between Molarity and Normality with Mass percentage (p)

If p is the mass percentage and d is the density of the solution then

$$\text{Molarity} = \frac{p \times d \times 10}{\text{Molecular mass (solute)}};$$

$$\text{Normality} = \frac{p \times d \times 10}{\text{Equivalent mass (solute)}}$$

8. Relationship between Molarity (M) and Molality (m)

$$m = \frac{1000 \times M}{(1000 \times d) - (M \times GMM_B)}$$

9. Relationship between Molality (m) and Mole fraction of solute (x_B)

$$x_B = \frac{m \times GMM_A}{1000 + m \times GMM_A}$$

$$\text{Also, } m = \frac{1000x_B}{x_A \times GMM_A}$$

10. **Dilution formula:** If the solution of some substance is diluted by adding solvent from volume V_1 to volume V_2 then

$$M_1 V_1 = M_2 V_2$$

Similarly,

$$N_1 V_1 = N_2 V_2$$

- 11. Molarity of a mixture:** If V_1 mL of a solution of molarity M_1 is mixed with another solution of same substance with volume V_2 and molarity M_2 then molarity of the resulting mixture of solution (M) can be obtained as:

$$M = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$$

- 12. Relationship between molarity (M) and mole fraction of solute (x_B)**

$$x_B = \frac{M \times GMM_A}{M(GMM_A - GMM_B) + 1000d}$$

Also,

$$M = \frac{1000 \times d \times x_B}{x_A \times GMM_A + x_B \times GMM_B}$$

- 13. Raoult's law for volatile solute**

$$p_A = p_A^\circ x_A \quad \text{and} \quad p_B = p_B^\circ x_B$$

where p_A and p_B are partial vapour pressures of component 'A' and component 'B' in the solution. p_A° and p_B° are vapour pressures of pure components 'A' and 'B' respectively.

$$\text{Total vapour pressure, } p = p_A + p_B = p_A^\circ x_A + p_B^\circ x_B$$

- 14. Raoult's law for non-volatile solute**

$$\frac{p_A^\circ - p}{p_A^\circ} = x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A} \quad (\text{For a dilute solution } n_B \ll n_A).$$

$$M_B = \left(\frac{p_A^\circ}{p_A^\circ - p_A} \right) \frac{W_B \times M_A}{W_A}$$

where x_B is mole fraction of solute and $\frac{p_A^\circ - p_A}{p_A^\circ}$ is relative lowering of vapour pressure.

- 15. Elevation in boiling point:**

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

$$\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A}$$

or,

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

where,

$$\Delta T_b = T_b - T_b^\circ$$

- 16. Depression in freezing point:**

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

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

or,

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

- 17. Osmotic pressure (π)**

$$\pi V = n_B RT$$

$$\pi V = \frac{W_B}{M_B} \times R \times T, \quad M_B = \frac{W_B \times R \times T}{\pi \times V}$$

$$\pi = \frac{n_B}{V} \times R \times T \quad \text{or} \quad \pi = CRT \quad \text{where 'C' is molarity.}$$

Osmotic pressure is related to the relative lowering of vapour pressure, elevation in boiling point and depression in freezing points according to the following relations:

$$\pi = \left(\frac{P_A^\circ - P_A}{P_A^\circ} \right) \times \frac{d \times R \times T}{M_B}$$

$$\pi = \frac{\Delta T_b \times d \times R \times T}{1000 \times K_b}$$

$$\pi = \frac{\Delta T_f \times d \times R \times T}{1000 \times K_f}$$

where d is the density of solution at temperature ' T '.

18. van't Hoff factor

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

or,

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

or,

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

Modified forms of colligative properties:

$$(a) \frac{P_A^\circ - P_A}{P_A^\circ} = i x_B$$

$$(b) \Delta T_b = i K_b m$$

$$(c) \Delta T_f = i K_f m$$

$$(d) \pi V = i n_B RT$$

19. $\alpha = \frac{i-1}{n-1}$, where α is degree of dissociation, ' i ' is van't Hoff factor, ' n ' is number of ions produced per formula of the compound.

20. $\alpha = \frac{1-i}{1-\frac{1}{n}}$ or $\alpha = \frac{i-1}{\frac{1}{n}-1}$

where α is degree of association, n is the number of molecules of solute that associate to form an associated molecule, $\frac{1}{n} < 1$.

21. Molal elevation constant, $K_b = \frac{R \times M_A \times (T_b^\circ)^2}{1000 \times \Delta_{\text{vap}} H}$

22. Molal depression constant, $K_f = \frac{R \times M_A \times (T_f^\circ)^2}{1000 \times \Delta_{\text{fus}} H}$

NCERT Textbook Questions

NCERT Intext Questions

- Q. 1.** Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

Ans. Mass percentage of benzene = $\frac{\text{Mass of benzene}}{\text{Mass of solution}} \times 100 = \frac{22\text{g}}{22\text{g} + 122\text{g}} \times 100 = 15.28\%$

Mass percentage of carbon tetrachloride = $100 - \text{Mass percentage of benzene}$
 $= 100 - 15.28 = 84.72\%$

Q. 2. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

Ans. Let the mass of solution be 100 g.

Mass of benzene = 30 g,

\therefore Mass of carbon tetrachloride = 100 g – 30 g = 70 g

$$\text{Number of moles of benzene} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{30 \text{ g}}{78 \text{ g mol}^{-1}} = 0.385 \text{ mol}$$

$$\text{Number of moles of carbon tetrachloride} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{70 \text{ g}}{154 \text{ g mol}^{-1}} = 0.455 \text{ mol}$$

$$\begin{aligned} \text{Mole fraction of benzene} &= \frac{\text{Moles of benzene}}{\text{Moles of benzene} + \text{Moles of carbon tetrachloride}} \\ &= \frac{0.385 \text{ mol}}{0.840 \text{ mol}} = \mathbf{0.458} \end{aligned}$$

Q. 3. Calculate the molarity of each of the following solutions:

(a) 30 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 4.3 L of solution

(b) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL

Ans. (a) Mass of solute, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ = 30 g

Molar mass of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ = $59 + 2(14 + 3 \times 16) + 6 \times 18 = 291 \text{ g mol}^{-1}$

$$\text{Number of moles of } \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{30 \text{ g}}{291 \text{ g mol}^{-1}} = 0.1 \text{ mol}$$

Volume of solution = 4.3 L

$$\text{Molarity of solution} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}} = \frac{0.1 \text{ mol}}{4.3 \text{ L}} = \mathbf{0.023 \text{ mol L}^{-1}}$$

(b) $M_1 = 0.5 \text{ M}$

$V_1 = 30 \text{ mL}$

$M_2 = ?$

$V_2 = 500 \text{ mL}$

Applying molarity equation, $M_1 V_1 = M_2 V_2$, we get

$$0.5 \text{ M} \times 30 \text{ mL} = M_2 \times 500 \text{ mL}$$

$$M_2 = \frac{0.5 \times 30 \text{ M}}{500} = \mathbf{0.03 \text{ M}}$$

Alternatively,

Number of moles = Molarity \times Volume of solution in litres

Number of moles of H_2SO_4 present in 0.5 M of 30 mL H_2SO_4 solution

$$= 0.5 \text{ mol L}^{-1} \times 0.03 \text{ L} = 0.015 \text{ mol}$$

$$\text{Volume of solution} = 500 \text{ mL} = \frac{500 \text{ L}}{1000} = 0.5 \text{ L}$$

$$\therefore \text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}} = \frac{0.015 \text{ mol}}{0.5 \text{ L}} = \mathbf{0.03 \text{ mol L}^{-1}}$$

Q. 4. Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution.

Ans. Mass of required aqueous solution = 2.5 kg = 2500 g

0.25 molal aqueous solution of urea means 0.25 mole of urea is dissolved in 1000 grams of water.

Mass of water = 1000 g

Moles of urea = 0.25 mol

Molar mass of urea (H_2NCONH_2) = $4 \times 1 + 2 \times 14 + 1 \times 12 + 1 \times 16 = 60 \text{ g mol}^{-1}$

Mass of urea = Number of moles of urea \times Molar mass of urea

$$\therefore \text{Mass of 0.25 moles of urea} = 0.25 \text{ mol} \times 60 \text{ g mol}^{-1} = 15 \text{ g}$$

$$\text{Mass of solution} = 1000 \text{ g} + 15 \text{ g} = 1015 \text{ g}$$

$$1015 \text{ g of aqueous solution contains urea} = 15 \text{ g}$$

$$\therefore 2500 \text{ g of aqueous solution will require urea} = \frac{15 \text{ g}}{1015 \text{ g}} \times 2500 \text{ g} = \mathbf{36.95 \text{ g}}$$

Q. 5. Calculate (i) molality (ii) molarity and (iii) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1} .

Ans. 20% (mass/mass) aqueous KI solution means that

$$\text{Mass of KI} = 20 \text{ g}$$

$$\text{Mass of solution} = 100 \text{ g}$$

$$\therefore \text{Mass of solvent (water)} = 100 - 20 = 80 \text{ g}$$

(i) Calculation of molality

$$\text{Molar mass of KI} = 39 + 127 = 166 \text{ g mol}^{-1}$$

$$n_{\text{KI}} = \frac{20 \text{ g}}{166 \text{ g mol}^{-1}} = 0.120$$

$$\text{Molality of solution} = \frac{n_{\text{KI}}}{W_{\text{H}_2\text{O}}} \times 1000 = \frac{0.120}{80} \times 1000 = \mathbf{1.5 \text{ m}}$$

(ii) Calculation of molarity

$$\text{Density of solution} = 1.202 \text{ g mL}^{-1}$$

$$\text{Volume of solution} = \frac{100 \text{ g}}{1.202 \text{ g mL}^{-1}} = 83.2 \text{ mL} = 0.0832 \text{ L}$$

$$\text{Molarity of solution} = \frac{n_{\text{KI}}}{\text{Volume of solution in L}} = \frac{0.120 \text{ mol}}{0.0832 \text{ L}} = \mathbf{1.44 \text{ M}}$$

Alternatively,

$$\text{Molarity} = \frac{\text{mass/mass \%} \times d \times 10}{\text{Molar mass of KI}} = \frac{20 \times 1.202 \times 10}{166} = \frac{240.4}{166} = \mathbf{1.45 \text{ M}}$$

(iii) Calculation of mole fraction of KI

$$n_{\text{KI}} = 0.120 \text{ mol}$$

$$n_{\text{H}_2\text{O}} = \frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{80 \text{ g}}{18 \text{ g mol}^{-1}} = 4.44 \text{ mol}$$

$$x_{\text{KI}} = \frac{n_{\text{KI}}}{n_{\text{H}_2\text{O}} + n_{\text{KI}}} = \frac{0.120 \text{ mol}}{4.44 \text{ mol} + 0.12 \text{ mol}} = \frac{0.120 \text{ mol}}{4.560 \text{ mol}} = \mathbf{0.0263}$$

Q. 6. H_2S , a toxic gas with rotten egg-like smell, is used for qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m , calculate Henry's law constant.

Ans. 0.195 m aqueous solution of H_2S means 0.195 mole of H_2S is dissolved in 1000 g of water.

$$\text{Number of moles of water in } 1000 \text{ g} = \frac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.55 \text{ mol}$$

$$\text{Number of moles of } \text{H}_2\text{S} = 0.195 \text{ mol}$$

$$x_{\text{H}_2\text{S}} = \frac{n_{\text{H}_2\text{S}}}{n_{\text{H}_2\text{S}} + n_{\text{H}_2\text{O}}} = \frac{0.195 \text{ mol}}{0.195 \text{ mol} + 55.55 \text{ mol}} = \frac{0.195 \text{ mol}}{55.745 \text{ mol}} = 0.0035$$

$$\text{According to Henry's law, } p_{\text{H}_2\text{S}} = K_{\text{H}} \times x_{\text{H}_2\text{S}}$$

$$\therefore 0.987 \text{ bar} = K_{\text{H}} \times 0.0035$$

$$K_{\text{H}} = \frac{0.987 \text{ bar}}{0.0035} = \mathbf{282 \text{ bar}}$$

Q. 7. Henry's law constant for CO_2 in water is $1.67 \times 10^8 \text{ Pa}$ at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

Ans. $p_{\text{CO}_2} = 2.5 \text{ atm} = 2.5 \times 10^5 \text{ Pa}$

$$K_H = 1.67 \times 10^8 \text{ Pa}$$

According to Henry's law,

$$p_{\text{CO}_2} = K_H \times x_{\text{CO}_2}$$

$$\therefore x_{\text{CO}_2} = \frac{p_{\text{CO}_2}}{K_H} = \frac{2.5 \times 10^5 \text{ Pa}}{1.67 \times 10^8 \text{ Pa}}$$

$$= 1.5 \times 10^{-3}$$

...(i)

$$\text{Mass of water} = \text{Density of water} \times \text{Volume of water}$$

$$= 1 \text{ g/mL} \times 500 \text{ mL} = 500 \text{ g}$$

Number of moles of water, ($n_{\text{H}_2\text{O}}$)

$$= \frac{\text{Mass of water}}{\text{Molar mass}} = \frac{500 \text{ g}}{18 \text{ g/mol}} = 27.78 \text{ mol}$$

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}} + n_{\text{CO}_2}} = \frac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}}}$$

\Rightarrow

$$\begin{aligned} n_{\text{CO}_2} &= x_{\text{CO}_2} \times n_{\text{H}_2\text{O}} \\ &= 1.5 \times 10^{-3} \times 27.78 \text{ mol} \\ &= 41.67 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\text{Mass of } \text{CO}_2 = \text{Number of moles of } \text{CO}_2 \times \text{Molar mass}$$

$$= 41.67 \times 10^{-3} \text{ mol} \times 44 \text{ g/mol}$$

$$= \mathbf{1.834 \text{ g}}$$

Q. 8. The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively at 350 K. Find out the composition of the liquid mixture if the total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

Ans. According to Raoult's law,

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= p_A^0 x_A + p_B^0 (1 - x_A) = p_B^0 + (p_A^0 - p_B^0) x_A$$

Here, $p_A^0 = 450 \text{ mm Hg}$; $p_B^0 = 700 \text{ mm Hg}$; $p = 600 \text{ mm Hg}$

Substituting the values, we get

$$600 = 700 + (450 - 700)x_A$$

$$250x_A = 100$$

$$\text{or } x_A = \frac{100}{250} = \mathbf{0.4}$$

Also,

$$x_A + x_B = 1$$

$$\text{or } x_B = 1 - x_A = 1 - 0.4 = \mathbf{0.6}$$

$$p_A = p_A^0 x_A$$

$$\text{and } p_B = p_B^0 x_B$$

$$p_A = 450 \text{ mm Hg} \times 0.4$$

$$\text{and } p_B = 700 \text{ mm Hg} \times 0.6$$

$$p_A = 180 \text{ mm Hg}$$

$$\text{and } p_B = 420 \text{ mm Hg}$$

In vapour phase,

$$\text{Mole fraction of A, } y_A = \frac{p_A}{p_A + p_B} = \frac{180 \text{ mm Hg}}{180 \text{ mm Hg} + 420 \text{ mm Hg}} = \mathbf{0.30}$$

$$\text{Mole fraction of B, } y_B = \frac{p_B}{p_A + p_B} = \frac{420 \text{ mm Hg}}{180 \text{ mm Hg} + 420 \text{ mm Hg}} = \mathbf{0.70}$$

Q. 9. Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea NH_2CONH_2 is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

Ans. Here, $p_A^0 = 23.8$ mm Hg

$$W_B = 50 \text{ g}, M_B (\text{urea}) = 60 \text{ g mol}^{-1}$$

$$W_A = 850 \text{ g}, M_A (\text{water}) = 18 \text{ g mol}^{-1}$$

Applying Raoult's law,

$$\begin{aligned} \frac{p_A^0 - p_s}{p_A^0} &= \frac{n_B}{n_A + n_B} = \frac{W_B/M_B}{W_A/M_A + W_B/M_B} \\ &= \frac{50/60}{850/18 + 50/60} \\ &= \frac{0.83}{47.22 + 0.83} = \frac{0.83}{48.05} = 0.017 \end{aligned}$$

Thus, relative lowering of vapour pressure = **0.017**

Substituting $p_A^0 = 23.8$ mm Hg, we get

$$\frac{23.8 - p_s}{23.8} = 0.017$$

On solving we get,

$$p_s = 23.40 \text{ mm Hg}$$

Hence, vapour pressure of water in the solution is **23.4 mm Hg**.

Q. 10. Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C?

Ans. Molecular mass of sucrose, $(\text{C}_{12}\text{H}_{22}\text{O}_{11})$, $M_B = 12 \times 12 + 22 \times 1 + 11 \times 16 = 342 \text{ g mol}^{-1}$

Mass of water = 500 g

Elevation in boiling point, $\Delta T_b = 100^\circ\text{C} - 99.63^\circ\text{C} = 0.37^\circ\text{C} = 0.37 \text{ K}$

$$\begin{aligned} \Delta T_b &= \frac{K_b \times W_B \times 1000}{M_B \times W_A} \Rightarrow W_B = \frac{\Delta T_b \times M_B \times W_A}{1000 \times K_b} \\ W_B &= \frac{0.37 \times 342 \times 500}{1000 \times 0.52} = 122 \text{ g} \end{aligned}$$

Q. 11. Calculate the mass of ascorbic acid (Vitamin C, $\text{C}_6\text{H}_8\text{O}_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. $K_f = 3.9 \text{ K kg mol}^{-1}$. [CBSE 2020 (56/1/1)]

Ans. Molecular mass of ascorbic acid, $M_B = 6 \times 12 + 8 \times 1 + 6 \times 16 = 176 \text{ g mol}^{-1}$

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

$$\begin{aligned} \text{or } W_B &= \frac{\Delta T_f \times M_B \times W_A}{K_f \times 1000} \\ &= \frac{1.5 \times 176 \times 75}{3.9 \times 1000} = 5.08 \text{ g} \end{aligned}$$

Q. 12. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

Ans. $\pi = CRT = \frac{n_B}{V} RT$...(i)

$$\text{Number of moles of solute dissolved, } n_B = \frac{1.0 \text{ g}}{185,000 \text{ g mol}^{-1}} = \frac{1}{185,000} \text{ mol}$$

$$V = 450 \text{ mL} = 0.450 \text{ L}$$

$$T = 37^\circ\text{C} = 37 + 273 = 310 \text{ K}$$

$$R = 8.314 \text{ kPa K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^3 \text{ Pa L K}^{-1} \text{ mol}^{-1}$$

Substituting these values in (i), we get

$$\pi = \frac{1}{185,000} \text{ mol} \times \frac{1}{0.45 \text{ L}} \times 8.314 \times 10^3 \text{ Pa L K}^{-1} \text{ mol}^{-1} \times 310 \text{ K}$$

$$= 30.96 \text{ Pa}$$

NCERT Textbook Exercises

Q. 1. Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.

Ans. Refer to Basic Concepts Points 1 and 2.

Q. 2. Give an example of a solid solution in which the solute is a gas.

Ans. Solution of hydrogen in palladium

Q. 3. Define the following terms

(i) mole fraction

(ii) molality

(iii) molarity

(iv) mass percentage

Ans. Refer to Basic Concepts Point 3.

Q. 4. Concentrated nitric acid used in the laboratory is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL⁻¹?

Ans. Consider 100 g sample of HNO₃ solution. As solution is 68% (m/m),

∴ Mass of nitric acid = 68 g

Molar mass of HNO₃ = 63 g mol⁻¹

∴ Number of moles of solute, HNO₃ = $\frac{68}{63} \text{ mol} = 1.079 \text{ mol}$

Density of solution = 1.504 g mL⁻¹

∴ Volume of solution = $\frac{\text{Mass}}{\text{Density}} = \frac{100 \text{ g}}{1.504 \text{ g mL}^{-1}} = 66.5 \text{ mL} = 0.0665 \text{ L}$

Molarity of the solution = $\frac{\text{Moles of the solute}}{\text{Volume of solution in L}} = \frac{1.079 \text{ mol}}{0.0665 \text{ L}} = 16.23 \text{ mol L}^{-1}$

Alternatively,

Molarity of the solution = $\frac{\text{mass/mass \%} \times d \times 10}{\text{Molar mass of HNO}_3} = \frac{68 \times 1.504 \times 10}{63} = \frac{1022.723}{63} = 16.23 \text{ M}$

Q. 5. A solution of glucose in water is labelled as 10 per cent w/w. What would be the molality and mole fraction of each component in the solution? If the density of the solution is 1.2 g mL⁻¹, what shall be the molarity of the solution? [CBSE (AI) 2014]

Ans. 10% w/w solution of glucose means 10 grams of glucose is present in 100 g of solution, i.e., 90 g of water.

Number of moles of glucose = $\frac{10 \text{ g}}{180 \text{ g mol}^{-1}} = 0.0555 \text{ mol}$

Number of moles of water = $\frac{90 \text{ g}}{18 \text{ g mol}^{-1}} = 5 \text{ mol}$

Molality of the solution = $\frac{\text{Number of moles of glucose}}{\text{Mass of water (in kg)}} = \frac{0.0555}{0.09 \text{ kg}} = 0.61 \text{ mol kg}^{-1}$

Mole fraction of glucose, $x_{\text{C}_6\text{H}_{12}\text{O}_6} = \frac{n_{\text{C}_6\text{H}_{12}\text{O}_6}}{n_{\text{C}_6\text{H}_{12}\text{O}_6} + n_{\text{H}_2\text{O}}} = \frac{0.055 \text{ mol}}{5 \text{ mol} + 0.055 \text{ mol}} = 0.01$

Mole fraction of water, $x_{\text{H}_2\text{O}} = 1 - x_{\text{C}_6\text{H}_{12}\text{O}_6} = 1.00 - 0.01 = 0.99$

Volume of 100 g glucose solution = $\frac{\text{Mass of solution}}{\text{Density of solution}}$

$$= \frac{100 \text{ g}}{1.2 \text{ g mL}^{-1}} = \frac{1000}{12} \text{ mL} = \frac{1}{12} \text{ L}$$

$$\text{Molarity of the solution} = \frac{\text{Number of moles of glucose}}{\text{Volume of solution}} = \frac{0.055 \text{ mol}}{\frac{1}{12} \text{ L}} = 0.660 \text{ mol L}^{-1}$$

Q. 6. How many mL of a 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and NaHCO_3 containing equimolar amounts of both?

Ans. To calculate the number of moles of the components in the mixture.

Let Na_2CO_3 present in the mixture be x g

$\therefore \text{NaHCO}_3$ present in the mixture = $(1 - x)$ g.

Molar mass of $\text{Na}_2\text{CO}_3 = 2 \times 23 + 12 + 3 \times 16 = 106 \text{ g mol}^{-1}$

Molar mass of $\text{NaHCO}_3 = 23 + 1 + 12 + 3 \times 16 = 84 \text{ g mol}^{-1}$

$$\therefore n_{\text{Na}_2\text{CO}_3} = \frac{x}{106} \text{ mol}, n_{\text{NaHCO}_3} = \frac{1-x}{84} \text{ mol}$$

As mixture contains equimolar amounts of the two,

$$\therefore \frac{x}{106} = \frac{1-x}{84} \quad \text{or} \quad 106 - 106x = 84x$$

$$\text{or} \quad x = \frac{106}{190} = 0.558 \text{ g}$$

$$\text{Thus, moles of } \text{Na}_2\text{CO}_3 = \frac{0.558}{106} = 0.00526$$

$$\text{Moles of } \text{NaHCO}_3 = \frac{1 - 0.558}{84} = \frac{0.442}{84} = 0.00526$$

To calculate the moles of HCl required.



1 mole of Na_2CO_3 requires HCl = 2 moles

\therefore 0.00526 mole of Na_2CO_3 requires HCl = 0.00526×2 moles = 0.01052 mole

1 mole of NaHCO_3 requires HCl = 1 mole

\therefore 0.00526 mole of NaHCO_3 requires HCl = 0.00526 mole

\therefore Total HCl required = 0.01052 mol + 0.00526 mole = 0.01578 mole

To calculate volume of 0.1 M HCl.

0.1 mole of 0.1 M HCl are present in 1000 mL of HCl.

$$0.01578 \text{ mole of } 0.1 \text{ M HCl will be present in HCl} = \frac{1000}{0.1} \times 0.01578 = 157.8 \text{ mL}$$

Q. 7. A solution is obtained by mixing 300 g of 25% and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

$$\text{Ans. } 300 \text{ g of } 25\% \text{ solution contains solute} = \frac{300 \times 25}{100} = 75 \text{ g}$$

$$400 \text{ g of } 40\% \text{ solution contains solute} = \frac{400 \times 40}{100} = 160 \text{ g}$$

$$\text{Total mass of solute} = 160 \text{ g} + 75 \text{ g} = 235 \text{ g}$$

$$\text{Total mass of solution} = 300 \text{ g} + 400 \text{ g} = 700 \text{ g}$$

$$\% \text{ of solute in the final solution} = \frac{235}{700} \times 100 = 33.5\%$$

$$\% \text{ of solvent in the final solution} = 100 - 33.5 = 66.5\%$$

Q. 8. An antifreeze solution is prepared from 222.6 g of ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2$ and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1} , then what shall be the molarity of the solution?

Ans. Mass of ethylene glycol = 222.6 g

Molar mass of ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2 = 62 \text{ g mol}^{-1}$

$$\text{Number of moles of ethylene glycol} = \frac{222.6 \text{ g}}{62 \text{ g mol}^{-1}} = 3.59 \text{ mol}$$

$$\text{Mass of water} = 200 \text{ g} = 0.20 \text{ kg}$$

$$\text{Molality of solution} = \frac{\text{Moles of ethylene glycol}}{\text{Mass of solvent (in kg)}} = \frac{3.59 \text{ mol}}{0.20 \text{ kg}} = 17.95 \text{ mol kg}^{-1}$$

$$\text{Total mass of the solution} = 222.6 \text{ g} + 200 \text{ g} = 422.6 \text{ g}$$

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}} = \frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}} = 394.2 \text{ mL} = 0.3942 \text{ L}$$

$$\text{Molarity of solution} = \frac{\text{Moles of ethylene glycol}}{\text{Volume of solution (in L)}} = \frac{3.59 \text{ mol}}{0.3942 \text{ L}} = 9.1 \text{ mol L}^{-1}$$

Q. 9. A sample of drinking water was found to be severely contaminated with chloroform, CHCl_3 which is supposed to be a carcinogen. The level of contamination was 15 ppm (by mass).

(i) Express this in percent by mass.

(ii) Determine the molality of chloroform in the water sample.

Ans. Let the mass of solution be 10^6 g .

Mass of solute, chloroform = 15 g

$$(i) \% \text{ by mass of chloroform} = \frac{\text{Mass of chloroform}}{\text{Mass of solution}} \times 100$$

$$= \frac{15 \text{ g}}{10^6 \text{ g}} \times 100 = 15 \times 10^{-4} \%$$

(ii) Mass of solvent, water = $10^6 \text{ g} - 15 \text{ g} \approx 10^6 \text{ g} \approx 10^3 \text{ kg}$

$$\begin{aligned} \text{Number of moles of chloroform, } \text{CHCl}_3 &= \frac{\text{Mass of chloroform}}{\text{Molar mass}} \\ &= \frac{15 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.126 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Molality of solution} &= \frac{\text{Number of moles of chloroform}}{\text{Mass of water (in kg)}} = \frac{0.126 \text{ mol}}{10^3 \text{ kg}} \\ &= 1.26 \times 10^{-4} \text{ mol kg}^{-1} \end{aligned}$$

Q. 10. What role molecular interaction play in the solution of alcohol and water?

Ans. There is intermolecular hydrogen bonding in alcohol as well as in water. On mixing, the magnitude of attractive forces tends to decrease. Due to decrease in attractive forces, the solution shows positive deviations from ideal behaviour. As a result, the solution will have higher vapour pressure and lower boiling point as compared to that of pure water and pure alcohol separately.

Q. 11. Why do gases always tend to be less soluble in liquid as the temperature is raised?

Ans. Gas + Liquid \rightleftharpoons Dissolved gas; $\Delta H = -ve$

Dissolution of gas in liquid is an exothermic process. As the temperature is increased, according to the Le Chatelier's principle the equilibrium will shift backward. This results in decrease of solubility of gases in liquid.

Q. 12. State Henry's law and mention some important applications.

Ans. Refer to Basic Concepts Point 2(c).

Q. 13. The partial pressure of ethane over a solution containing $6.56 \times 10^{-3} \text{ g}$ of ethane is 1 bar. If the solution contains $5.00 \times 10^{-2} \text{ g}$ of ethane, then what shall be the partial pressure of the gas?

Ans. According to Henry's law, $m = K_H \times p$

$$\text{Case I.} \quad 6.56 \times 10^{-3} \text{ g} = K_H \times 1 \text{ bar}$$

$$\text{or,} \quad K_H = 6.56 \times 10^{-3} \text{ g bar}^{-1}$$

Case II. $5.00 \times 10^{-2} \text{ g} = (6.56 \times 10^{-3} \text{ g bar}^{-1}) \times p$

or
$$p = \frac{5.00 \times 10^{-2} \text{ g}}{6.56 \times 10^{-3} \text{ g bar}^{-1}} = 7.62 \text{ bar}$$

Q. 14. What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{\text{mix}}H$ related to positive and negative deviations from Raoult's law?

Ans. Refer to Basic Concepts Point 5(b).

Q. 15. An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?

Ans. Vapour pressure of pure water at the boiling point (p°) = 1 atm = 1.013 bar

Vapour pressure of solution (p_s) = 1.004 bar

Mass of solute, $W_B = 2 \text{ g}$

Mass of solution = 100 g

Mass of solvent, $W_A = 100 \text{ g} - 2 \text{ g} = 98 \text{ g}$

Applying Raoult's law for dilute solution (being 2%)

$$\frac{p_A^\circ - p_s}{p_A^\circ} = x_B = \frac{n_B}{n_A + n_B} \simeq \frac{n_B}{n_A} = \frac{W_B/M_B}{W_A/M_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$$\frac{(1.013 \text{ bar} - 1.004 \text{ bar})}{1.013 \text{ bar}} = \frac{2 \text{ g} \times 18 \text{ g mol}^{-1}}{M_B \times 98 \text{ g}}$$

or
$$M_B = \frac{2 \text{ g} \times 18 \text{ g mol}^{-1} \times 1.013 \text{ bar}}{98 \text{ g} \times 0.009 \text{ bar}} = 41.35 \text{ g mol}^{-1}$$

Q. 16. Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa, respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35.0 g of octane?

Ans. Molar mass of heptane, $\text{C}_7\text{H}_{16} = 100 \text{ g mol}^{-1}$

Molar mass of octane, $\text{C}_8\text{H}_{18} = 114 \text{ g mol}^{-1}$

$$n_{\text{C}_7\text{H}_{16}} = \frac{26.0 \text{ g}}{100 \text{ g mol}^{-1}} = 0.26 \text{ mol}$$

$$n_{\text{C}_8\text{H}_{18}} = \frac{35.0 \text{ g}}{114 \text{ g mol}^{-1}} = 0.31 \text{ mol}$$

$$x_{\text{C}_7\text{H}_{16}} = \frac{n_{\text{C}_7\text{H}_{16}}}{n_{\text{C}_7\text{H}_{16}} + n_{\text{C}_8\text{H}_{18}}} = \frac{0.26}{0.26 + 0.31} = 0.456$$

$$x_{\text{C}_8\text{H}_{18}} = 1 - x_{\text{C}_7\text{H}_{16}} = 1 - 0.456 = 0.544$$

$$p_{\text{C}_7\text{H}_{16}} = 105.2 \text{ kPa} \times 0.456 = 47.97 \text{ kPa}$$

$$p_{\text{C}_8\text{H}_{18}} = 46.8 \text{ kPa} \times 0.544 = 25.46 \text{ kPa}$$

$$p_{\text{total}} = p_{\text{C}_7\text{H}_{16}} + p_{\text{C}_8\text{H}_{18}} = 47.97 + 25.46 = 73.43 \text{ kPa}$$

Q. 17. The vapour pressure of water is 12.3 kPa at 300 K. Calculate the vapour pressure of 1 molal solution of a non-volatile solute in it.

Ans. 1 molal solution means 1 mol of the solute is present in 1000 g of the solvent, H_2O (assuming the solution to be dilute).

$$n_{\text{H}_2\text{O}} = \frac{1000}{18} = 55.5 \text{ mol}$$

$$x_{\text{solute}} = \frac{1}{1 + 55.5} = 0.0177$$

Also,
$$x_{\text{solute}} = \frac{p_A^o - p_s}{p_A^o} \Rightarrow 0.0177 = \frac{12.3 - p_s}{12.3}$$

or
$$p_s = 12.08 \text{ kPa}$$

Q. 18. Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80% .

Ans. $p_s = 80\% \text{ of } p^o = \frac{80 \times p^o}{100} = 0.80 p^o; n_B = \frac{W_B}{40} \text{ mol}$

$$n_{\text{C}_8\text{H}_{18}} = \frac{114 \text{ g}}{114 \text{ g mol}^{-1}} = 1 \text{ mol (Molar mass of C}_8\text{H}_{18} = 114 \text{ g mol}^{-1})$$

Now,
$$\frac{p^o - p_s}{p^o} = x_B$$

$$\frac{p^o - 0.80p^o}{p^o} = \frac{n_B}{n_B + n_{\text{C}_8\text{H}_{18}}} = \frac{W_B/40}{W_B/40 + 1}$$

$$0.2 \left(\frac{W_B}{40} + 1 \right) = \frac{W_B}{40} \quad \text{or} \quad \frac{0.8 W_B}{40} = 0.2$$

or
$$W_B = 10 \text{ g}$$

Q. 19. A solution containing 30 g of a non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K . Further 18 g of water is then added to the solution, the new vapour pressure becomes 2.9 kPa at 298 K . Calculate (i) molar mass of the solute (ii) vapour pressure of water at 298 K .

Ans. (i) Suppose the molar mass of the solute = $M_B \text{ g mol}^{-1}$

Number of moles of solute, $n_B = \frac{30}{M_B} \text{ mol}$

Number of solvent (water), $n_A = \frac{90 \text{ g}}{18 \text{ g mol}^{-1}} = 5 \text{ mol}$

According to Raoult's law,

$$\frac{p_A^o - p_s}{p_A^o} = \frac{n_B}{n_A + n_B}, \text{ i.e., } \frac{p_A^o - 2.8}{p_A^o} = \frac{30/M_B}{5 + (30/M_B)}$$

or
$$1 - \frac{2.8}{p_A^o} = \frac{30/M_B}{5 + (30/M_B)}$$

or
$$\frac{2.8}{p_A^o} = 1 - \frac{30/M_B}{5 + (30/M_B)} = \frac{5 + 30/M_B - 30/M_B}{5 + (30/M_B)} = \frac{5}{5 + (30/M_B)}$$

or
$$\frac{p_A^o}{2.8} = \frac{5 + (30/M_B)}{5} = 1 + \frac{6}{M_B} \quad \dots(i)$$

After adding 18 g of water,

Number of moles of water (n_A) = $\frac{108}{18} = 6 \text{ mol}$

According to Raoult's law,

$\therefore \frac{p_A^o - 2.9}{p_A^o} = \frac{30/M_B}{6 + (30/M_B)}$

or
$$1 - \frac{2.9}{p_A^o} = \frac{30/M_B}{6 + (30/M_B)}$$

$$\text{or } \frac{2.9}{p_A^0} = 1 - \frac{30/M_B}{6 + (30/M_B)} = \frac{6 + (30/M_B) - (30/M_B)}{6 + (30/M_B)} = \frac{6}{6 + (30/M_B)}$$

$$\text{or } \frac{p_A^0}{2.9} = \frac{6 + (30/M_B)}{6}$$

$$\text{or } \frac{p_A^0}{2.9} = 1 + \frac{5}{M_B} \quad \dots(ii)$$

Dividing equation (i) by equation (ii), we get

$$\frac{2.9}{2.8} = \frac{1 + (6/M_B)}{1 + (5/M_B)}$$

$$\text{or } 2.9 \left(1 + \frac{5}{M_B}\right) = 2.8 \left(1 + \frac{6}{M_B}\right)$$

$$\text{or } 2.9 + \frac{14.5}{M_B} = 2.8 + \frac{16.8}{M_B} \quad \text{or } \frac{2.3}{M_B} = 0.1 \quad \text{or } M_B = 23 \text{ g mol}^{-1}$$

(ii) Putting the value of M_B in equation (i), we get

$$\frac{p_A^0}{2.8} = 1 + \frac{6}{23} = \frac{29}{23}$$

$$\text{or } p_A^0 = \frac{29}{23} \times 2.8 = 3.53 \text{ kPa}$$

Q. 20. A 5% solution (by mass) of cane sugar in water has a freezing point of 271 K. Calculate the freezing point of a 5% glucose in water if the freezing point of pure water is 273.15 K.

Ans. Let the mass of solution = 100 g

\therefore Mass of the cane sugar = 5 g

Mass of solvent, water = 100 g – 5 g = 95 g

$\Delta T_f = 273.15 \text{ K} - 271 \text{ K} = 2.15 \text{ K}$

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

$$K_f = \frac{2.15 \times 342 \times 95}{5 \times 1000} = 13.97 \text{ K kg mol}^{-1}$$

For 5% solution of glucose in water

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A} = \frac{13.97 \times 5 \times 1000}{180 \times 95}$$

$$\Delta T_f = 4.08 \text{ K}$$

Freezing point of glucose solution, $T_f = \Delta T_f^0 - \Delta T_f = 273.15 \text{ K} - 4.08 \text{ K} = 269.07 \text{ K}$

Q. 21. Two elements A and B form compounds having molecular formula AB_2 and AB_4 . When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molal depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. Calculate atomic masses of A and B.

Ans. We know,

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

$$\therefore M_{AB_2} = \frac{5.1 \times 1 \times 1000}{2.3 \times 20} = 110.87 \text{ g mol}^{-1}$$

$$\text{Similarly, } M_{AB_4} = \frac{5.1 \times 1 \times 1000}{1.3 \times 20} = 196.15 \text{ g mol}^{-1}$$

Suppose atomic masses of A and B are 'a' and 'b' respectively. Then

Molar mass of $AB_2 = a + 2b = 110.87 \text{ g mol}^{-1} \dots(i)$

Molar mass of $AB_4 = a + 4b = 196.15 \text{ g mol}^{-1} \dots(ii)$

Subtracting equation (i) from equation (ii), we get

$$2b = 85.28 \text{ or } b = 42.64$$

Substituting the value of b in equation (i), we get

$$a + 2 \times 42.64 = 110.87 \text{ or } a = 25.59$$

Thus, Atomic mass of $A = 25.59 \text{ u}$

Atomic mass of $B = 42.64 \text{ u}$

Q. 22. At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?

Ans. Osmotic pressure, $\pi = CRT$

First case:

$$\text{Number of moles of glucose, } C_6H_{12}O_6 = \frac{36 \text{ g}}{180 \text{ g mol}^{-1}} = 0.2 \text{ mol}$$

$$\text{Molar concentration of solution, } C = \frac{0.2 \text{ mol}}{1 \text{ L}} = 0.2 \text{ mol L}^{-1}$$

$$\therefore 4.98 \text{ bar} = 0.2 \text{ mol L}^{-1} \times R \times 300 \text{ K} \quad \dots(i)$$

Second case:

$$1.52 = C \times R \times 300 \text{ K} \quad \dots(ii)$$

Dividing equation (ii) by equation (i), we get

$$\frac{1.52 \text{ bar}}{4.98 \text{ bar}} = \frac{C \times R \times 300 \text{ K}}{0.2 \text{ mol L}^{-1} \times R \times 300 \text{ K}}$$

$$0.305 = \frac{C}{0.2 \text{ mol L}^{-1}}$$

or

$$C = 0.0610 \text{ mol L}^{-1}$$

Q. 23. Suggest the most important type of intermolecular interaction in the following pairs:

(i) *n*-hexane and *n*-octane (ii) I_2 and CCl_4 (iii) $NaClO_4$ and water (iv) methanol and acetone (v) acetonitrile (CH_3CN) and acetone (C_3H_6O).

Ans. (i) Dispersion or London forces as both are non-polar.

(ii) Dispersion or London forces as both are non-polar.

(iii) Ion-dipole interactions as sodium chlorate gives Na^+ and ClO_4^- ions and water is a polar molecule.

(iv) Dipole-dipole interactions as both are polar molecules.

(v) Dipole-dipole interactions as both are polar molecules.

Q. 24. Based on solute-solvent interactions, arrange the following in order of increasing solubility in *n*-octane and explain.

Cyclohexane, KCl, CH_3OH , CH_3CN

Ans. (i) Cyclohexane and *n*-octane both are non-polar. Hence, they will mix completely in all proportions.

(ii) KCl is an ionic compound whereas *n*-octane is non-polar. Hence, KCl will not dissolve at all in *n*-octane.

(iii) CH_3OH and CH_3CN both are polar but CH_3CN is less polar than CH_3OH . As *n*-octane is non-polar, CH_3CN will dissolve more than CH_3OH in *n*-octane.

Therefore, the order of solubility in *n*-octane will be $KCl < CH_3OH < CH_3CN < \text{Cyclohexane}$.

Q. 25. Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water: (i) phenol, (ii) toluene, (iii) formic acid, (iv) ethylene glycol, (v) chloroform, (vi) pentanol.

Ans. (i) Partially soluble as it has non-polar C_6H_5 group and polar $-OH$ group which can form hydrogen bond with water.

(ii) Insoluble as toluene is non-polar while water is polar.

- (iii) Highly soluble as formic acid can form hydrogen bonds with water.
- (iv) Highly soluble as ethylene glycol can form hydrogen bonds with water.
- (v) Insoluble as chloroform despite its polarity, cannot form hydrogen bonds with water.
- (vi) Partially soluble as —OH group is polar but the bulky C₅H₁₁ part is non-polar.

Q. 26. If the density of some lake water is 1.25 g mL⁻¹ and contains 92 g of Na⁺ ions per kg of water, calculate the molality of Na⁺ ions in the lake.

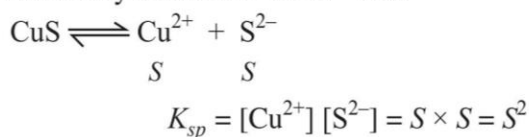
Ans. Number of moles of Na⁺ ion = $\frac{92 \text{ g}}{23 \text{ g mol}^{-1}} = 4 \text{ mol}$

$$\begin{aligned}\text{Molality of Na}^+ \text{ ions} &= \frac{\text{Number of moles of Na}^+ \text{ ions}}{\text{Mass of water in kg}} \\ &= \frac{4 \text{ mol}}{1 \text{ kg}} = 4 \text{ mol kg}^{-1} = \mathbf{4 \text{ m}}\end{aligned}$$

Q. 27. If the solubility product of CuS is 6×10^{-16} , calculate the maximum molarity of CuS in aqueous solution.

Ans. Maximum molarity of CuS in aqueous solution = Solubility of CuS in mol L⁻¹.

If S is the solubility of CuS in mol L⁻¹ then



$$\therefore S^2 = 6 \times 10^{-16}$$

$$\text{or } S = \sqrt{6 \times 10^{-16}} = \mathbf{2.45 \times 10^{-8} \text{ mol L}^{-1}}$$

$$\text{Maximum molarity of CuS in aqueous solution} = \mathbf{2.45 \times 10^{-8} \text{ mol L}^{-1}}$$

Q. 28. Calculate the mass percentage of aspirin (C₉H₈O₄) in acetonitrile (CH₃CN) when 6.5 g of C₉H₈O₄ is dissolved in 450 g of CH₃CN.

Ans. Mass of solution = 6.5 g + 450 g = 456.5 g

$$\text{Mass \% of aspirin} = \frac{\text{Mass of aspirin}}{\text{Mass of solution}} \times 100 = \frac{6.5}{456.5} \times 100 = \mathbf{1.424\%}$$

Q. 29. Nalorphene (C₁₉H₂₁NO₃) similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of $1.5 \times 10^{-3} \text{ m}$ aqueous solution required for the above dose.

Ans. $1.5 \times 10^{-3} \text{ m}$ solution means that 1.5×10^{-3} mole of nalorphene is dissolved in 1 kg of water.

$$\text{Molar mass of C}_{19}\text{H}_{21}\text{NO}_3 = 19 \times 12 + 21 + 14 + 48 = 311 \text{ g mol}^{-1}$$

$$1.5 \times 10^{-3} \text{ mole of C}_{19}\text{H}_{21}\text{NO}_3 = 1.5 \times 10^{-3} \times 311 \text{ g} = 0.467 \text{ g}$$

$$\therefore \text{Mass of solution} = 1000 \text{ g} + 0.467 \text{ g} = 1000.467 \text{ g}$$

$$\therefore \text{Thus, for 0.467 g of nalorphene, solution required} = 1000.467 \text{ g}$$

$$\text{Hence, for } 1.5 \times 10^{-3} \text{ g of nalorphene, solution required} = \frac{1000.467 \text{ g}}{0.467} \times 1.5 \times 10^{-3} \text{ g} = \mathbf{3.21 \text{ g}}$$

Q. 30. Calculate the amount of benzoic acid (C₆H₅COOH) required for preparing 250 mL of 0.15 mol L⁻¹ solution in methanol.

Ans.
$$\text{Molarity} = \frac{\text{Mass of solute/Molar mass}}{\text{Volume of solution (in litres)}}$$

$$\text{Mass of benzoic acid} = \text{Molarity} \times \text{Volume of solution} \times \text{Molar mass}$$

$$\text{Volume of solution} = 250 \text{ mL} = \frac{250}{1000} \text{ L} = 0.25 \text{ L}$$

$$\text{Molar mass of benzoic acid, C}_6\text{H}_5\text{COOH} = 7 \times 12 + 6 \times 1 + 2 \times 16 = 122 \text{ g mol}^{-1}$$

$$\text{Mass of benzoic acid} = 0.15 \text{ mol L}^{-1} \times 0.25 \text{ L} \times 122 \text{ g mol}^{-1} = \mathbf{4.575 \text{ g}}$$

Q. 31. The depression in freezing point of water observed for the same amount of acetic acid, tri-chloroacetic acid and trifluoroacetic acid increases in the order as given. Explain briefly.

Ans. The depression in freezing points are in the order:



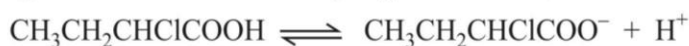
Fluorine, being the most electronegative, has the highest negative inductive effect. As a result of this, trifluoroacetic acid is the strongest acid while acetic acid is the weakest acid. Hence, trifluoroacetic acid ionises to the largest extent while acetic acid ionises to the minimum extent to give ions in their solutions in water. Greater the ions produced, greater is the depression in freezing point. Hence, the depression in freezing point is the maximum for the trifluoroacetic acid and minimum for acetic acid.

Q. 32. Calculate the depression in the freezing point of water when 10 g of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$ is added to 250 g of water; $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86 \text{ K kg mol}^{-1}$.

Ans. Number of moles of $\text{CH}_3\text{CH}_2\text{CHClCOOH} = \frac{10 \text{ g}}{122.5 \text{ g mol}^{-1}} = 8.16 \times 10^{-2} \text{ mol}$

$$\begin{aligned} \text{Molality of the solution} &= \frac{\text{No. of moles of solute}}{\text{Mass of solvent (in grams)}} \times 1000 \\ &= \frac{8.16 \times 10^{-2}}{250} \times 1000 = 0.3264 \text{ mol kg}^{-1} \end{aligned}$$

If α is the degree of dissociation of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$, then



Initial conc. $C \text{ mol L}^{-1}$ 0 0

At equilibrium $C(1 - \alpha)$ $C\alpha$ $C\alpha$

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = C\alpha^2 \quad [\text{Considering } (1 - \alpha) = 1 \text{ for dilute solution}]$$

or
$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$$

Calculation of van't Hoff factor:



Initial moles 1 0 0

Moles at equilibrium $1 - \alpha$ α α

Total number of mole of particles after dissociation $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$i = \frac{\text{Total number of moles of particles after dissociation}}{\text{Number of particles before dissociation}}$$

or,
$$i = \frac{1 + \alpha}{1} = 1 + \alpha = 1 + 0.065 = 1.065$$

$\therefore \Delta T_f = i K_f m$
 $= (1.065) (1.86) (0.3264) = 0.65 \text{ K}$

Q. 33. 19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point observed is 1.0°C . Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

OR

When 19.5 g of $\text{F}-\text{CH}_2-\text{COOH}$ (Molar mass $= 78 \text{ g mol}^{-1}$) is dissolved in 500 g of water, the depression in freezing point is observed to be 1°C . Calculate the degree of dissociation of $\text{F}-\text{CH}_2-\text{COOH}$.

(Given: K_f of water $= 1.86 \text{ K kg mol}^{-1}$)

[CBSE 2020 (56/3/1)]

Ans. Calculation of van't Hoff factor (i):

Number of moles of fluoroacetic acid $= \frac{19.5 \text{ g}}{78 \text{ g mol}^{-1}} = 0.25 \text{ mol}$

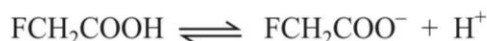
$$\text{Molality, } m = \frac{\text{Number of moles of fluoroacetic acid}}{\text{Mass of water in kg}} = \frac{0.25 \text{ mol}}{0.5 \text{ kg}} = 0.5 \text{ mol kg}^{-1}$$

$$\Delta T_f = i \times K_f \times m \Rightarrow i = \frac{\Delta T_f}{K_f \times m}$$

Here, $\Delta T_f = 1.0 \text{ K}$; $K_f = 1.86 \text{ K kg mol}^{-1}$; $m = 0.5 \text{ mol kg}^{-1}$

$$i = \frac{1.0 \text{ K}}{1.86 \text{ K kg mol}^{-1} \times 0.5 \text{ mol kg}^{-1}} = 1.0753$$

Calculation of dissociation constant, K_a :



Initial conc.	0.5	0	0
At equilibrium	$0.5(1 - \alpha)$	0.5α	0.5α

$$\text{Total} = 0.5(1 + \alpha)$$

$$i = \frac{0.5(1 + \alpha)}{0.5} = 1 + \alpha \quad \text{or} \quad \alpha = i - 1 = 1.0753 - 1 = 0.0753$$

$$K_a = \frac{0.5\alpha + 0.5\alpha}{0.5(1 - \alpha)} = \frac{0.5\alpha^2}{1 - \alpha} = \frac{0.5 \times (0.0753)^2}{1 - 0.0753}$$

$$K_a = 3.07 \times 10^{-3}$$

Q. 34. Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water.

Ans. $p_A^0 = 17.535 \text{ mm Hg}$; $W_B = 25 \text{ g}$; $W_A = 450 \text{ g}$

$M_B = 180 \text{ g mol}^{-1}$; $M_A = 18 \text{ g mol}^{-1}$

Substituting the values in the expression

$$\frac{p_A^0 - p_s}{p_A^0} = \frac{W_B \times M_A}{M_B \times W_A}, \text{ we get}$$

$$\frac{17.535 - p_s}{17.535} = \frac{25 \times 18}{180 \times 450} \quad \text{or} \quad 1 - \frac{p_s}{17.535} = \frac{1}{180}$$

$$\frac{179}{180} = \frac{p_s}{17.535} \quad \text{or} \quad p_s = 17.44 \text{ mm Hg}$$

Q. 35. Henry's law constant for the molality of methane in benzene at 298 K is $4.27 \times 10^5 \text{ mm Hg}$. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

Ans. Here, $K_H = 4.27 \times 10^5 \text{ mm Hg}$,

$$p = 760 \text{ mm Hg}$$

According to Henry's law, $p = K_H \times x_{\text{CH}_4}$

$$\therefore x_{\text{CH}_4} = \frac{p}{K_H} = \frac{760 \text{ mm Hg}}{4.27 \times 10^5 \text{ mm Hg}} = 1.78 \times 10^{-3}$$

Mole fraction of methane in benzene, $x_{\text{CH}_4} = 1.78 \times 10^{-3}$

Q. 36. 100 g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 torr.

Ans. $n_A = \frac{100 \text{ g}}{140 \text{ g mol}^{-1}} = \frac{5}{7} \text{ mol}$ and $n_B = \frac{1000 \text{ g}}{180 \text{ g mol}^{-1}} = \frac{50}{9} \text{ mol}$

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

$$\therefore x_A = \frac{5/7}{5/7 + 50/9} = \frac{5/7}{395/63} = \frac{5}{7} \times \frac{63}{395} = \frac{45}{395} = 0.114$$

$$\therefore x_B = 1 - 0.114 = 0.886$$

Also, given $P_B^0 = 500$ torr

According to Raoult's law,

$$p_A = x_A p_A^0 = 0.114 \times p_A^0$$

...(i)

$$p_B = x_B p_B^0 = 0.886 \times 500 = 443 \text{ torr}$$

$$P = p_A + p_B$$

$$475 = 0.114 p_A^0 + 443$$

$$\text{or } p_A^0 = \frac{475 - 443}{0.114} = \mathbf{280.7 \text{ torr}}$$

Substituting this value in equation (i), we get

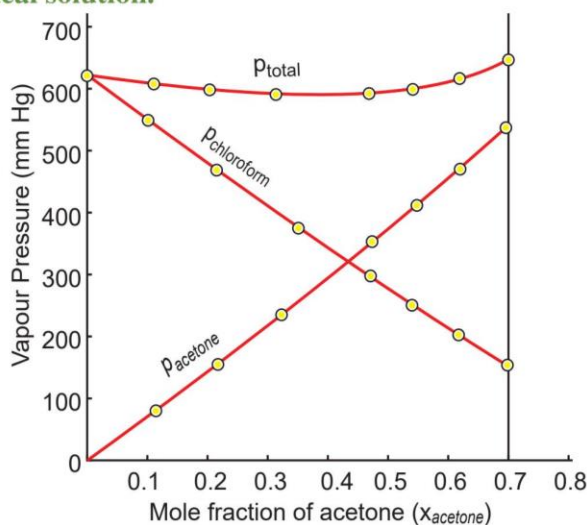
$$P_A = 280.7 \times 0.114 = \mathbf{32 \text{ torr}}$$

Q. 37. Vapour pressures of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total} , $p_{\text{chloroform}}$ and p_{acetone} as a function of x_{acetone} , the experimental data observed for different compositions of mixture is:

$100 \times x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{\text{acetone}} / \text{mm Hg}$	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}} / \text{mm Hg}$	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

Ans.



x_{acetone}	0	0.118	0.234	0.360	0.508	0.582	0.645	0.721
$p_{\text{acetone}} / \text{mm Hg}$	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}} / \text{mm Hg}$	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7
p_{total}	632.8	603.0	579.5	562.1	580.4	599.5	615.3	641.8

Since the plot for p_{total} dips downwards, the solution shows negative deviation from the ideal behaviour.

Q. 38. Benzene and toluene form ideal solution over the entire range of composition. The vapour pressures of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in the vapour phase if 80 g of benzene is mixed with 100 g of toluene.

Ans. Molar mass of benzene (C_6H_6) = 78 g mol⁻¹

Molar mass of toluene (C_7H_8) = 92 g mol⁻¹

$$n_{\text{C}_6\text{H}_6} = \frac{80 \text{ g}}{78 \text{ g mol}^{-1}} = 1.026 \text{ mol}$$

$$n_{C_7H_8} = \frac{100}{92 \text{ g mol}^{-1}} = 1.087 \text{ mol}$$

$$\therefore x_{C_6H_6} = \frac{n_{C_6H_6}}{n_{C_6H_6} + n_{C_7H_8}} = \frac{1.026}{1.026 + 1.087} = \frac{1.026}{2.113} = 0.486$$

$$x_{C_7H_8} = 1 - 0.486 = 0.514$$

$$p_{C_6H_6}^0 = 50.71 \text{ mm Hg}, p_{C_7H_8}^0 = 32.06 \text{ mm Hg}$$

Applying Raoult's law

$$p_{C_6H_6} = x_{C_6H_6} \times p_{C_6H_6}^0 = 0.486 \times 50.71 \text{ mm Hg} = 24.65 \text{ mm Hg}$$

$$p_{C_7H_8} = x_{C_7H_8} \times p_{C_7H_8}^0 = 0.514 \times 32.06 \text{ mm Hg} = 16.48 \text{ mm Hg}$$

$$\therefore \text{Mole fraction of benzene in the vapour phase} = \frac{p_{C_6H_6}}{p_{C_6H_6} + p_{C_7H_8}} = \frac{24.65}{24.65 + 16.48} = \frac{24.65}{41.13} = 0.60$$

Q. 39. The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K, if the Henry's law constants for oxygen and nitrogen at 298 K are $3.30 \times 10^7 \text{ mm}$ and $6.51 \times 10^7 \text{ mm}$ respectively, calculate the composition of these gases in water.

Ans. Partial pressure of oxygen, $p_{O_2} = \frac{20}{100} \times 10 \text{ atm} = 2 \text{ atm} = 2 \times 760 \text{ mm Hg} = 1520 \text{ mm Hg}$

Partial pressure of nitrogen, $p_{N_2} = \frac{79}{100} \times 10 \text{ atm} = 7.9 \text{ atm} = 7.9 \times 760 \text{ mm Hg} = 6004 \text{ mm Hg}$

$$K_H(O_2) = 3.30 \times 10^7 \text{ mm}, K_H(N_2) = 6.51 \times 10^7 \text{ mm}$$

Applying Henry's law, $p_{O_2} = K_H \times x_{O_2}$

or $x_{O_2} = \frac{p_{O_2}}{K_H} = \frac{1520 \text{ mm}}{3.30 \times 10^7 \text{ mm}} = 4.61 \times 10^{-5}$

$$p_{N_2} = K_H \times x_{N_2}$$

or $x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{6004 \text{ mm}}{6.51 \times 10^7 \text{ mm}} = 9.22 \times 10^{-5}$

Q. 40. Determine the amount of CaCl_2 ($i = 2.47$) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27°C .

Ans. $\pi = \frac{i \times W_B \times R \times T}{M_B \times V}$ or $W_B = \frac{\pi \times M_B \times V}{i \times R \times T}$

Molar mass of CaCl_2 , $M_B = 40 + 2 \times 35.5 = 111 \text{ g mol}^{-1}$

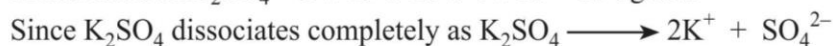
$$\text{Mass of } \text{CaCl}_2, W_B = \frac{0.75 \text{ atm} \times 111 \text{ g mol}^{-1} \times 2.5 \text{ L}}{2.47 \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} = 3.42 \text{ g}$$

Q. 41. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25°C , assuming that it is completely dissociated. [CBSE Delhi 2013, 2019 (56/5/2)]

Ans. K_2SO_4 dissolved = 25 mg = 0.025 g

Volume of solution = 2 L, $T = 25^\circ\text{C} = 298 \text{ K}$

Molar mass of $\text{K}_2\text{SO}_4 = 2 \times 39 + 32 + 4 \times 16 = 174 \text{ g mol}^{-1}$



$$i = \frac{\text{Number of moles of particles after dissociation}}{\text{Number of moles of particles before dissociation}} = \frac{3}{1} = 3$$

Applying van't Hoff equation,

$$\pi = \frac{i \times W_B \times R \times T}{M_B \times V}$$

$$= \frac{3 \times 0.025 \text{ g} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{174 \text{ g mol}^{-1} \times 2 \text{ L}} = 5.27 \times 10^{-3} \text{ atm}$$

Multiple Choice Questions

[1 mark]

Choose and write the correct option(s) in the following questions.

- A solution of amalgam of mercury with sodium contains

Solute	Solvent	Solute	Solvent
(a) Solid	Solid	(b) Solid	Liquid
(c) Liquid	Solid	(d) Liquid	Liquid
- One kilogram of sea water sample contains 6 mg of dissolved O_2 . The concentration of O_2 in ppm in the sample is

(a) 0.06	(b) 60	(c) 6	(d) 0.6
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- Mole fraction of the solute in a 1.0 molal aqueous solution is:

(a) 0.1770	(b) 0.0177	(c) 0.0344	(d) 1.7700
------------	------------	------------	------------
- At what concentration does the solution of ethylene glycol used as an antifreeze?

(a) 35% volume by volume	(b) 35% mass by volume
(c) 35% mass by mass	(d) 35 ppm
- On dissolving sugar in water at room temperature solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid? [NCERT Exemplar]

(a) Sugar crystals in cold water.	(b) Sugar crystals in hot water.
(c) Powdered sugar in cold water.	(d) Powdered sugar in hot water.
- At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is _____. [NCERT Exemplar]

(a) less than the rate of crystallisation	(b) greater than the rate of crystallisation
(c) equal to the rate of crystallisation	(d) zero
- Which of the following factor(s) affect the solubility of a gaseous solute in the fixed volume of liquid solvent? [NCERT Exemplar]

(i) nature and solute	(ii) temperature	(iii) pressure
(a) (i) and (iii) at constant T	(b) (i) and (ii) at constant P	
(c) (ii) and (iii) only	(d) (iii) only	
- The value of Henry's constant K_H is _____. [NCERT Exemplar]

(a) greater for gases with higher solubility.	(b) greater for gases with lower solubility.
(c) constant for all gases.	(d) not related to the solubility of gases.
- Low concentration of oxygen in the blood and tissues of people living at high altitude is due to _____. [NCERT Exemplar]

(a) low temperature	(b) low atmospheric pressure
(c) high atmospheric pressure	(d) both low temperature and high atmospheric pressure
- A solution of chloroform in diethylether:

(a) obeys Raoult's law	(b) shows a positive deviation from Raoult's law
(c) shows a negative deviation from Raoult's law	(d) behaves like a near ideal solution
- Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law? [NCERT Exemplar]

(a) Methanol and acetone.	(b) Chloroform and acetone.
(c) Nitric acid and water.	(d) Phenol and aniline.

12. Intermolecular forces between two benzene molecules are nearly of same strength as those between two toluene molecules. For a mixture of benzene and toluene, which of the following are not true? [NCERT Exemplar]
- (a) $\Delta_{mix}H = \text{zero}$ (b) $\Delta_{mix}V = \text{zero}$
(c) These will form minimum boiling azeotrope (d) These will not form ideal solution
13. The system that forms maximum boiling azeotropes is:
- (a) ethyl alcohol-water (b) benzene-toluene
(c) acetone-chloroform (d) carbon disulphide-acetone
14. At a given temperature, osmotic pressure of a concentrated solution of a substance _____. [NCERT Exemplar]
- (a) is higher than that of a dilute solution.
(b) is lower than that of a dilute solution.
(c) is same as that of a dilute solution.
(d) cannot be compared with osmotic pressure of dilute solution.
15. An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because _____. [NCERT Exemplar]
- (a) it gains water due to osmosis. (b) it loses water due to reverse osmosis.
(c) it gains water due to reverse osmosis. (d) it loses water due to osmosis.
16. If we place the blood cells in a solution containing less than 0.9% (m/V) sodium chloride. They would swell. This is because
- (a) the solution is hypotonic (b) the solution is isotonic
(c) the solution is hypertonic (d) none of these
17. Which of the following colligative property is used to calculate the molar mass of biomolecules?
- (a) Relative lowering of vapour pressure (b) Elevation in boiling point
(c) Depression in freezing point (d) Osmotic pressure
18. Which of the following statements is false? [NCERT Exemplar]
- (a) Units of atmospheric pressure and osmotic pressure are the same.
(b) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration.
(c) The value of molal depression constant depends on nature of solvent.
(d) Relative lowering of vapour pressure, is a dimensionless quantity.
19. The values of Van't Hoff factors for KCl, NaCl and K_2SO_4 , respectively, are _____. [NCERT Exemplar]
- (a) 2, 2 and 2 (b) 2, 2 and 3 (c) 1, 1 and 2 (d) 1, 1 and 1
20. The value of van't Hoff factor for ethanoic acid in benzene is
- (a) 1.0 (b) 1.5 (c) 0.5 (d) 2
21. Which of the following aqueous solutions should have the highest boiling point? [NCERT Exemplar]
- (a) 1.0 M NaOH (b) 1.0 M Na_2SO_4 (c) 1.0 M NH_4NO_3 (d) 1.0 M KNO_3
22. In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M $MgCl_2$ solution is _____. [NCERT Exemplar]
- (a) the same (b) about twice (c) about three times (d) about six times
23. Molal elevation constant is calculated from the enthalpy of vapourisation ($\Delta_{vap}H$) and boiling point of the pure solvent (T_0) using the relation:
- (a) $K_b = \frac{M_A RT_0^2}{1000 \Delta_{vap}H}$ (b) $K_b = \frac{1000 RT_0^2}{M_A \Delta_{vap}H}$
(c) $K_b = \frac{\Delta_{vap}H}{1000 M_A RT_0^2}$ (d) $K_b = \frac{1000 M_A T_0^2}{\Delta_{vap}HR}$

24. Which of the following statements is false?

[NCERT Exemplar]

- (a) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.
- (b) The osmotic pressure of a solution is given by the equation $\pi = CRT$ (where C is the molarity of the solution).
- (c) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is

$$\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{sucrose}.$$
- (d) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution.

Answers

1. (c) 2. (c) 3. (b) 4. (a) 5. (d) 6. (c) 7. (a), (b) 8. (b) 9. (b) 10. (c)
 11. (a) 12. (c), (d) 13. (c) 14. (a) 15. (d) 16. (a) 17. (d) 18. (b) 19. (b) 20. (c)
 21. (b) 22. (c) 23. (d) 24. (a)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
- (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
- (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
- (d) Assertion (A) is incorrect, but Reason (R) is correct statement.

- Assertion (A) :** Molarity of a solution in liquid state changes with temperature.
Reason (R) : The volume of a solution changes with change in temperature.
- Assertion (A) :** The solubility of a gas in a liquid increases with increase of pressure.
Reason (R) : The solubility of a gas in a liquid is directly proportional to the pressure of the gas.
- Assertion (A) :** Raoult's law is a special case of Henry's law.
Reason (R) : Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.
- Assertion (A) :** Non-ideal solutions always form azeotropes.
Reason (R) : Boiling point of an azeotrope may be higher or lower than boiling points of both components.
- Assertion (A) :** If more volatile liquid is added to another liquid, vapour pressure of solution will be greater than that of pure solvent.
Reason (R) : Vapour pressure of solution is entirely due to solvent molecules.
- Assertion (A) :** The vapour pressure of a liquid decreases if some non-volatile solute is dissolved in it.
Reason (R) : The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.
- Assertion (A) :** The boiling point of pure solvent is always higher than the boiling point of solution.
Reason (R) : The vapour pressure of the solvent decreases in the presence of non-volatile solute.
- Assertion (A) :** When NaCl is added to water a depression in freezing point is observed.
Reason (R) : The lowering of vapour pressure of a solution causes depression in the freezing point.

- 9. Assertion (A) :** When a solution is separated from the pure solvent by a semipermeable membrane, the solvent molecules pass through it from pure solvent side to the solution side.
Reason (R) : Diffusion of solvent occurs from a region of high concentration solution to a region of low concentration solution.
- 10. Assertion (A) :** Lowering of vapour pressure is directly proportional to osmotic pressure of the solution.
Reason (R) : Osmotic pressure is a colligative property.
- 11. Assertion (A) :** Molecular mass of polymers cannot be calculated using boiling point or freezing point method.
Reason (R) : Polymers solutions do not possess a constant boiling point or freezing point.
- 12. Assertion (A) :** The boiling point of 0.1 M urea solution is less than that of 0.1 M KCl solution.
Reason (R) : Elevation of boiling point is directly proportional to the number of species present in the solution.

Answers

1. (a) 2. (a) 3. (b) 4. (d) 5. (c) 6. (b) 7. (d) 8. (a) 9. (c) 10. (b)
11. (c) 12. (a)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE-1

The spontaneous flow of the solvent through a semipermeable membrane from a pure solvent to a solution or from a dilute solution to a concentrated solution is called osmosis. The phenomenon of osmosis can be demonstrated by taking two eggs of the same size. In an egg, the membrane below the shell and around the egg material is semi-permeable. The outer hard shell can be removed by putting the egg in dilute hydrochloric acid. After removing the hard shell, one egg is placed in distilled water and the other in a saturated salt solution. After some time, the egg placed in distilled water swells-up while the egg placed in salt solution shrinks.

The external pressure applied to stop the osmosis is termed as osmotic pressure (a Colligative property). Reverse osmosis takes place when the applied external pressure becomes larger than the osmotic pressure.

- What do you expect to happen when red blood corpuscles (RBC's) are placed in 0.5% NaCl solution?**
Ans. RBC's are isotonic with 0.9% NaCl solution, so they will swell and may even burst when placed in 0.5% NaCl solution.
- Which one of the following will have higher osmotic pressure in 1 M KCl or 1 M urea solution?**
Ans. 1 M KCl will have higher osmotic pressure because it dissociates to give K^+ and Cl^- ions while urea does not dissociate into ions in the solution.
- Name one SPM which can be used in the process of reverse osmosis.**
Ans. Cellulose acetate placed on a suitable support.
- What are isotonic solutions?**
Ans. Solutions having equal osmotic pressure are called isotonic solutions.
- Write van't Hoff equation for dilute solution.**
Ans. $\pi V = nRT$,

Where, π = Osmotic pressure, n = Number of moles, V = Volume of solution in litre, R = Gas constant, T = Temperature

PASSAGE-2

A solution which obeys Raoult's law strictly is called an ideal solution, while a solution which shows deviations from Raoult's law is called a non-ideal solution or real solution. Suppose the molecules of the solvent and solute are represented by A and B respectively, and let γ_{AB} , γ_{AA} and γ_{BB} are the attractive forces between $A-B$, $A-A$ and $B-B$ respectively. An ideal solution of the components A and B is defined as the solution in which the intermolecular interactions between the components $A-B$ are of the same magnitude as the intermolecular interactions found in the pure components $A-A$ and $B-B$. Similarly, a non-ideal solution of the components A and B is defined as the solution in which the intermolecular interactions between the components $A-B$ are of the different magnitude as the intermolecular interactions found in the pure components $A-A$ and $B-B$.

1. What type of liquids form the ideal solution?

Ans. Liquids that have similar structures and polarities form ideal solutions.

2. Give one example of an ideal solution.

Ans. Benzene + Toluene

3. Write two characteristics of non-ideal solution.

Ans. $\Delta H_{\text{mix}} \neq 0$, $\Delta V_{\text{mix}} \neq 0$.

4. On mixing liquid A and liquid B, volume of the resulting solution decreases, what type of deviation from Raoult's law is shown by?

Ans. The solution will show negative deviation from Raoult's law.

5. Which type of deviation will be shown by the solution, if $\gamma_{AB} < \gamma_{AA}$?

Ans. Solution will show positive deviation.

Very Short Answer Questions

[1 mark]

Q. 1. Define mole fraction.

[CBSE Delhi 2012]

Ans. Mole fraction of a component in a solution may be defined as the ratio of moles of that component to the total number of moles of all the components present in the solution.

Q. 2. How does the molarity of a solution change with temperature?

Ans. Molarity decreases with increase in temperature as volume of solution increases with increase in temperature.

Q. 3. When and why is molality preferred over molarity in handling solutions in chemistry?

Ans. Molality is preferred in studies that involves changes in temperature as in some of the colligative properties of solutions. This is because molality depends on masses of solvent which do not change with temperature.

Q. 4. The dissolution of ammonium chloride in water is an endothermic process but still it dissolves in water readily. Why?

[HOTS]

Ans. This is because of entropy change. In this case, ΔS is +ve.



The ions that were held together in crystalline solid are free and moving in all possible directions. Its entropy has increased and this makes $T\Delta S > \Delta H$, i.e., $\Delta G = -ve$.

Q. 5. Why are the aquatic species more comfortable in cold water in comparison to warm water?

[CBSE 2019 (56/2/3), (56/4/1)]

Ans. At a given pressure, the solubility of oxygen in water increases with decrease in temperature. Presence of more oxygen at lower temperature makes the aquatic species more comfortable in cold water.

Q. 6. What is the similarity between Raoult's law and Henry's law?

[CBSE Delhi 2014]

Ans. The similarity between Raoult's law and Henry's law is that in both the laws, the partial vapour pressure of the volatile component or gas is directly proportional to its mole fraction in the solution.

Q. 7. What type of liquids form ideal solutions?

Ans. Liquids that have similar structures and polarities form ideal solutions.

Q. 8. Write two characteristics of non-ideal solution.

[CBSE 2019 (56/5/2)]

Ans. $\Delta_{mix} H \neq 0$ and $\Delta_{mix} V \neq 0$

Q. 9. Under what condition do non-ideal solutions show negative deviations?

Ans. When the new forces of interaction between the components are stronger than those in the pure components, then non-ideal solutions show negative deviations.

Q. 10. What are maximum boiling azeotropes? Give one example.

Ans. Maximum boiling azeotropes are those which boil at higher temperature than boiling point of each component in pure state, e.g., 68% nitric acid and 32% water by mass.

Q. 11. Why is the vapour pressure of a solution of glucose in water lower than that of water?

[NCERT Exemplar]

Ans. This is due to decrease in the escaping tendency of the water molecules from the surface of solution as some of the surface area is occupied by non-volatile solute, glucose particles.

Q. 12. Define molal depression constant or cryoscopic constant.

Ans. It is the depression in freezing point when 1 mole of non-volatile solute is dissolved in 1000 g of solvent.

Q. 13. What do you understand by the term that K_f for water is $1.86 \text{ K kg mol}^{-1}$?

Ans. It means that the freezing point of water is lowered by 1.86 K when 1 mole of non-volatile solute is dissolved in 1 kg of water.

Q. 14. What is an antifreeze?

Ans. A substance such as ethylene glycol which is added to water to lower its freezing point is called an antifreeze. It is named so as it delays freezing.

Q. 15. What is de-icing agent? How does it work?

Ans. Common salt is called de-icing agent as it lowers the freezing point of water to such an extent that it does not freeze to form ice. Thus, it is used to clear snow from roads.

Q. 16. Why is glycol and water mixture used in car radiators in cold countries?

[HOTS]

Ans. Ethylene glycol lowers the freezing point of water. Due to this, coolant in radiators will not freeze. Otherwise, radiator will burst due to freezing of coolant (water).

Q. 17. What are isotonic solutions?

[CBSE Delhi 2012, 2014]

Ans. The solutions of the same osmotic pressure at a given temperature are called isotonic solutions.

Q. 18. How is it that measurement of osmotic pressures is more widely used for determining molar masses of macromolecules than the elevation in boiling point or depression in freezing point of their solutions?

[CBSE (AI) 2009]

Ans. The osmotic pressure method has the advantage over elevation in boiling point or depression in freezing point for determining molar masses of macromolecules because

- (i) Osmotic pressure is measured at the room temperature and the molarity of solution is used instead of molality.
- (ii) Compared to other colligative properties, its magnitude is large even for very dilute solutions.

Q. 19. What is the van't Hoff factor for a compound which undergo dimerisation in an organic solvent?

Ans. $2X \longrightarrow X_2$

$$i = \frac{\text{Number of moles of particles after association}}{\text{Number of moles of particles before association}} = \frac{1}{2}$$

Q. 20. What would be the value of van't Hoff factor for a dilute solution of K_2SO_4 in water?

Ans. In dilute solution, $K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$

$$\text{van't Hoff factor, } i = \frac{\text{Number of moles of particles after dissociation}}{\text{Number of moles of particles before dissociation}} = \frac{3}{1} = 3.$$

Q. 21. Out of two 0.1 molal aqueous solutions of glucose and of potassium chloride, which one will have a higher boiling point and why?

[CBSE (F) 2013, 2019 (56/3/2)]

Ans. 0.1 m KCl solution will have higher boiling point as KCl dissociates in the solution.

Q. 22. What will happen to freezing point of a potassium iodide aqueous solution when mercuric iodide is added to solution? [HOTS]



Mercuric iodide forms a complex with potassium iodide, therefore, the number of solute particles (KI) in the solution decreases resulting in the decrease in the value of ΔT_f , i.e., depression in the freezing point. As a result, the freezing point ($T_f = T_f^\circ + \Delta T_f$) of the solution will increase.

Q. 23. Why is osmotic pressure of 1 M KCl higher than 1 M urea solution?

Ans. This is because KCl dissociates to give K^+ and Cl^- ions while urea being a molecular solid does not dissociate into ions in the solution.

Short Answer Questions-I

[2 marks]

Q. 1. Explain the solubility rule “like dissolves like” in terms of intermolecular forces that exist in solutions.

Ans. A substance (solute) dissolves in a solvent if the intermolecular interactions are similar in both the components; for example, polar solutes dissolve in polar solvents and non polar solutes in non polar solvents and thus we can say “like dissolves like”.

Q. 2. State Henry’s law. Write its one application. What is the effect of temperature on solubility of gases in liquid? [CBSE (F) 2016]

Ans. It states that the partial pressure of a gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

$$p \propto x \quad \text{or} \quad p = K_H x \quad \text{where } K_H \text{ is the Henry’s constant.}$$

Application of Henry’s law:

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

Effect of temperature on solubility:

As dissolution is an exothermic process, therefore, according to Le Chatelier’s principle solubility should decrease with rise in temperature.

Q. 3. Henry’s law constant (K_H) for the solution of methane in benzene at 298 K is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg. [CBSE (F) 2013]

Ans. Here, $K_H = 4.27 \times 10^5$ mm Hg, $p = 760$ mm Hg

According to Henry’s law, $p = K_H x_{\text{CH}_4}$

$$\therefore x_{\text{CH}_4} = \frac{p}{K_H} = \frac{760 \text{ mm Hg}}{4.27 \times 10^5 \text{ mm Hg}} = 1.78 \times 10^{-3}$$

Mole fraction of methane in benzene, $x_{\text{CH}_4} = 1.78 \times 10^{-3}$.

Q. 4. State Raoult’s law for the solution containing volatile components. What is the similarity between Raoult’s law and Henry’s law? [CBSE Delhi 2014; 2020 (56/5/1)]

Ans. It states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction. According to Raoult’s law, for a volatile component, A of the solution $P_A \propto x_A$ or $P_A = P_A^0 x_A$, where P_A^0 is the vapour pressure of pure component A.

If one of the component is so volatile that it exist as a gas then according to Henry’s law $p = K_H x$, where K_H is the Henry law constant i.e., the partial vapour pressure of the volatile component (gas) is directly proportional to its mole fraction in the solution.

Thus the similarity between Raoult’s law and Henry’s law is that in both the laws, the partial vapour pressure of the volatile component or gas is directly proportional to its mole fraction in the solution.

Q. 5. State the following:

(i) Raoult’s law in its general form in reference to solutions.

(ii) Henry’s law about partial pressure of a gas in a mixture.

[CBSE (AI) 2011]

Ans. (i) **Raoult’s law:** It states that for any solution, the partial pressure of each volatile component in the solution is directly proportional to its mole fraction.

(ii) **Henry’s law:** It states that the partial pressure of a gas in vapour phase (P) is proportional to its mole fraction (x) in the solution.

Q. 6. Define an ideal solution and write one of its characteristics.

[CBSE Delhi 2014]

Ans. A solution which obeys Raoult's law over the entire range of concentration is called ideal solution. The important characteristics of an ideal solution are

- (i) The enthalpy of mixing of pure components to form the solution is zero i.e., $\Delta_{\text{mix}}H = 0$
- (ii) The volume of mixing is zero i.e., $\Delta_{\text{mix}}V = 0$

Q. 7. State Raoult's law for the solution containing volatile components. Write two differences between an ideal solution and a non-ideal solution.

[CBSE Panchkula 2015]

Ans. Raoult's law states that for a solution of volatile liquids the partial vapour pressure of each component is directly proportional to its mole fraction.

Differences between Ideal and non-Ideal solutions

S.No.	Ideal solution	Non-Ideal solution
(i)	Obeys Raoult's law over entire range of concentration i.e., $P_A = P_A^\circ x_A$; $P_B = P_B^\circ x_B$	Does not obey Raoult's law over entire range of concentration, i.e., $P_A \neq P_A^\circ x_A$; $P_B \neq P_B^\circ x_B$
(ii)	$\Delta_{\text{mix}}H = 0$; $\Delta_{\text{mix}}V = 0$	$\Delta_{\text{mix}}H \neq 0$; $\Delta_{\text{mix}}V \neq 0$
(iii)	Does not form azeotrope.	Forms azeotrope.

(Any two)

Q. 8. Write two differences between a solution showing positive deviation and a solution showing negative deviation from Raoult's law.

[CBSE East 2016]

Ans.

Solutions showing positive deviation from Raoult's law	Solution showing negative deviation from Raoult's law
(i) $P_A > P_A^\circ x_A$ and $P_B > P_B^\circ x_B$	(i) $P_A < P_A^\circ x_A$ and $P_B < P_B^\circ x_B$
(ii) $\Delta_{\text{mix}}H > 0$, $\Delta_{\text{mix}}V > 0$	(ii) $\Delta_{\text{mix}}H < 0$, $\Delta_{\text{mix}}V < 0$
(iii) Form minimum boiling azeotropes.	(iii) Form maximum boiling azeotropes.

(Any two)

Q. 9. State Raoult's law for a solution containing non-volatile solute. What type of deviation from Raoult's law is shown by a solution of chloroform and acetone and why?

[CBSE (F) 2017]

Ans. It states that the relative lowering of vapour pressure is equal to mole fraction of solute when solvent alone is volatile and is expressed as

$$\frac{P_A^\circ - P_{\text{Total}}}{P_A^\circ} = x_B$$

A solution of chloroform and acetone shows negative deviation from Raoult's law. This is because chloroform molecule is able to form H-bond with acetone molecule as shown below.



It decreases the escaping tendency of molecules of each component from the surface of solution and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law.

Q. 10. (i) Why is an increase in temperature observed on mixing chloroform and acetone?

[CBSE 2019 (56/2/3)]

(ii) Why does sodium chloride solution freeze at a lower temperature than water? [CBSE (F) 2013]

- Ans.**
- (i) The bonds between chloroform molecules and molecules of acetone are dipole-dipole interactions but on mixing, the chloroform and acetone molecules, they start forming hydrogen bonds which are stronger bonds resulting in the release of energy. This gives rise to an increase in temperature.
 - (ii) When a non-volatile solute is dissolved in a solvent, the vapour pressure decreases. As a result, the solvent freezes at a lower temperature.

Q. 11. Define azeotropes. What type of azeotrope is formed by negative deviation from Raoult's law? Give an example.

[CBSE Delhi 2015]

Ans. Azeotropes are binary liquid mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.

Maximum boiling azeotrope is formed by negative deviation from Raoult's law. A mixture of 68% nitric acid and 32% water by mass is an example of maximum boiling azeotrope.

Q. 12. What type of deviation is shown by a mixture of ethanol and acetone? What type of azeotrope is formed by mixing ethanol and acetone? [CBSE (F) 2013]

Ans. A mixture of ethanol and acetone shows positive deviation and the azeotrope formed by this mixture is minimum boiling azeotrope.

Q. 13. (i) Gas (A) is more soluble in water than Gas (B) at the same temperature. Which one of the two gases will have the higher value of K_H (Henry's constant) and why?

(ii) In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes? [CBSE Central 2016]

Ans. (i) According to Henry's law, $p = K_H x$, i.e., higher the value of K_H lower is the solubility of the gas in the liquid. Therefore, Gas B will have higher value of K_H than gas A.

(ii) Negative deviation from Raoult's law.

Q. 14. Derive the relationship between relative lowering of vapour pressure and molar mass of the solute. [CBSE Chennai 2015]

Ans. From Raoult's law we have, $p = p_A + p_B$

If solute B is non-volatile, then

$$p = p_A \text{ or } p = p_A^\circ x_A$$

$$p = p_A^\circ (1 - x_B) = p_A^\circ - p_A^\circ x_B$$

$$p_A^\circ x_B = p_A^\circ - p$$

$$\frac{p_A^\circ - p}{p_A^\circ} = x_B \text{ or } \frac{\Delta p}{p_A^\circ} = \frac{n_B}{n_A + n_B}$$

For a dilute solution $n_B \ll n_A$, so n_B can be neglected in denominator in comparison to n_A .

$$\frac{\Delta p}{p_A^\circ} = \frac{n_B}{n_A} = \frac{W_B/M_B}{W_A/M_A} = \frac{W_B \times M_A}{M_B \times W_A}$$

$$M_B = \frac{p_A^\circ \times W_B \times M_A}{\Delta p \times W_A}$$

Q. 15. When 1.5 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point of benzene raised from 353.23 K to 353.93 K. Calculate the molar mass of the solute.

(K_b for benzene = 2.52 K kg mol⁻¹)

[CBSE Chennai 2015]

Ans. $\Delta T_b = 353.93 \text{ K} - 353.23 \text{ K} = 0.7 \text{ K}$

Substituting $W_B = 1.5 \text{ g}$, $W_A = 90 \text{ g}$, $\Delta T_b = 0.7 \text{ K}$, $K_b = 2.52 \text{ K kg mol}^{-1}$ in the expression

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}, \text{ we get}$$

$$M_B = \frac{2.52 \times 1.5 \times 1000}{0.7 \times 90}$$

$$M_B = 60 \text{ g mol}^{-1}$$

Q. 16. Calculate the freezing point of a solution containing 60 g of glucose (Molar mass = 180 g mol⁻¹) in 250 g of water. (K_f of water = 1.86 K kg mol⁻¹) [CBSE Delhi 2018]

Ans. Here, $W_B = 60 \text{ g}$, $M_B = 180 \text{ g mol}^{-1}$, $W_A = 250 \text{ g}$, $K_f = 1.86 \text{ K kg mol}^{-1}$

Substituting these values in the expression

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}, \text{ we get}$$

$$\Delta T_f = \frac{1.86 \times 60 \times 1000}{180 \times 250} = 2.48 \text{ K}$$

Freezing point of solution, $T_f = T_f^\circ - \Delta T_f = 273.15 \text{ K} - 2.48 \text{ K} = 270.67 \text{ K}$

Q. 17. Define the term osmotic pressure. Describe how the molecular mass of a substance can be determined by a method based on measurement of osmotic pressure. [CBSE Delhi 2012]

Ans. Osmotic pressure (π) is defined as the extra pressure that must be applied to the solution side in order to prevent the flow of solvent molecules into it through a semipermeable membrane.

According to van't Hoff equation

$$\pi = \frac{n_B}{V} RT$$

where π is the osmotic pressure, R is the gas constant and V is the volume of solution in litres containing n_B moles of the solute.

If W_B grams of the solute of molar mass, M_B is present in the solution, then

$$n_B = \frac{W_B}{M_B} \text{ and we can write}$$

$$\pi = \frac{W_B \times R \times T}{M_B \times V} \quad \text{or} \quad M_B = \frac{W_B \times R \times T}{\pi \times V}$$

Thus, knowing W_B , T , π and V , the molecular mass of the solute, M_B can be calculated.

Q. 18. A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming that the gene fragment is a non-electrolyte, calculate its molar mass. [CBSE (AI) 2011]

Ans. $M_B = \frac{W_B \times R \times T}{\pi \times V} \dots(i)$

Here, $W_B = 8.95 \text{ mg} = 8.95 \times 10^{-3} \text{ g}$, $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$

$$T = 25^\circ\text{C} = (25 + 273) \text{ K} = 298 \text{ K}, \pi = 0.335 \text{ torr} = \frac{0.335}{760} \text{ atm}$$

$$V = 35 \text{ mL} = 35 \times 10^{-3} \text{ L}$$

Substituting these values in the equation (i), we get

$$M_B = \frac{8.95 \times 10^{-3} \text{ g} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times 760}{0.335 \text{ atm} \times 35 \times 10^{-3} \text{ L}} = 14193.3 \text{ g mol}^{-1}$$

Q. 19. Give reasons: [CBSE 2019 (56/2/T)]

(i) **Cooking is faster in pressure cooker than in cooking pan.**

(ii) **Red Blood Cells (RBC) shrink when placed in saline water but swell in distilled water.**

Ans. (i) The use of pressure cooker reduces cooking time because the weight over the lid does not allow the steam to go out. As a result, pressure inside the cooker becomes high. Higher the pressure, higher is the boiling point and faster is the cooking.

(ii) As the concentration of saline solution is higher than the concentration inside the cell. Thus water will move outside the cytoplasm and the cell will shrink while, distilled water is hypotonic, when RBCs are placed in distilled water, water will enter the cell through simple diffusion and lead to cell swelling.

Q. 20. (i) On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution? What change in temperature would you observe after mixing liquids X and Y?

(ii) **What happens when we place the blood cell in water (hypotonic solution)? Give reason.** [CBSE Allahabad 2015]

Ans. (i) ● The solution will show negative deviation from Raoult's law.
● Temperature will rise.

(ii) Due to osmosis water enters into the cell and blood cell will swell.

Q. 21. Define the following terms:

(i) **Abnormal molar mass**

(ii) **van't Hoff factor (*i*)**

[CBSE Delhi 2017]

Ans. (i) When the molar mass of a substance determined by using any of the colligative properties comes out to be different than the theoretically expected molar mass, the substance said to show abnormal molar mass.

(ii) van't Hoff factor (*i*) gives the extent of association or dissociation of the solute particles in the solution. It may be defined as the ratio of observed colligative property to calculated colligative property.

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

Q. 22. Will the elevation in boiling point be same if 0.1 mol of sodium chloride or 0.1 mol of sugar is dissolved in 1 L of water? Explain.

[CBSE Sample Paper 2016] [HOTS]

Ans. No, the elevation in boiling point is not the same. NaCl, being an electrolyte, dissociates almost completely to give Na^+ and Cl^- ions whereas glucose, being non-electrolyte does not dissociate. Hence, the number of particles in 0.1 M NaCl solution is nearly double than 0.1 M glucose solution. Elevation in boiling point being a colligative property, is therefore, nearly twice for 0.1 M NaCl solution than for 0.1 M glucose solution.

Short Answer Questions-II

[3 marks]

Q. 1. At 25°C the saturated vapour pressure of water is 3.165 kPa (23.75 mm Hg). Find the saturated vapour pressure of a 5% aqueous solution of urea (carbamide) at the same temperature.

(Molar mass of urea = 60.05 g mol⁻¹)

[CBSE (F) 2012]

Ans. $W_B = 5$ g, $W_A = 95$ g, $M_B = 60.05$ g mol⁻¹, $M_A = 18$ g mol⁻¹, $p_A^0 = 3.165$ kPa

Substituting the values in the expression

$$\frac{p_A^0 - p}{p_A^0} = \frac{W_B \times M_A}{M_B \times W_A}, \text{ we get}$$

$$\frac{3.165 \text{ kPa} - p}{3.165 \text{ kPa}} = \frac{5 \text{ g} \times 18 \text{ g mol}^{-1}}{60.05 \text{ g mol}^{-1} \times 95 \text{ g}} = 0.015$$

$$p = 3.165 \text{ kPa} - 0.015 \times 3.165 \text{ kPa}$$

$$p = 3.118 \text{ kPa}$$

Q. 2. Calculate the boiling point of solution when 2 g of Na₂SO₄ (M = 142 g mol⁻¹) was dissolved in 50 g of water, assuming Na₂SO₄ undergoes complete ionisation.

(*K_b* for water = 0.52 K kg mol⁻¹)

[CBSE North 2016]

Ans. $i = \frac{3}{1} = 3$ ($\text{Na}_2\text{SO}_4 \longrightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$)

Given, $W_B = 2$ g, $W_A = 50$ g, $M_B = 142$ g mol⁻¹, $K_b = 0.52$ K kg mol⁻¹

Substituting the values in the expression, $\Delta T_b = \frac{i \times K_b \times W_B \times 1000}{M_B \times W_A}$

$$\Delta T_b = \frac{3 \times 0.52 \times 2 \times 1000}{142 \times 50} = 0.439 \text{ K}$$

So, boiling point of solution, $T_b = T_b^0 + \Delta T_b$

$$= 373.15 \text{ K} + 0.439 \text{ K} = 373.589 \text{ K}$$

Q. 3. A solution of glucose (Molar mass = 180 g mol⁻¹) in water has a boiling point of 100.20°C. Calculate the freezing point of the same solution. Molal constants for water *K_f* and *K_b* are 1.86 K kg mol⁻¹ and 0.512 K kg mol⁻¹ respectively.

[CBSE (F) 2017]

Ans. $\Delta T_b = 100.20^\circ\text{C} - 100^\circ\text{C} = 0.20^\circ\text{C}$ or 0.20 K

$$\Delta T_b = K_b \cdot m \quad \Rightarrow \quad m = \Delta T_b / K_b$$

$$m = \frac{0.20 \text{ K}}{0.512 \text{ K kg mol}^{-1}} \text{ or } m = 0.39 \text{ mol kg}^{-1}$$

$$\Delta T_f = K_f m$$

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 0.39 \text{ mol kg}^{-1} = 0.725 \text{ K}$$

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

$$= 273.15 \text{ K} - 0.725 \text{ K} = \mathbf{272.425 \text{ K}}$$

Q. 4. Calculate the freezing point of a solution when 3 g of CaCl_2 ($M = 111 \text{ g mol}^{-1}$) was dissolved in 100 g of water, assuming CaCl_2 undergoes complete ionisation. (K_f for water = $1.86 \text{ K kg mol}^{-1}$)

[CBSE East 2016]

Ans. Here, $W_B = 3 \text{ g}$, $i = \frac{3}{1} = 3$ ($\text{CaCl}_2 \rightarrow \text{Ca}^{2+} + 2\text{Cl}^-$), $W_A = 100 \text{ g}$, $K_f = 1.86 \text{ K kg mol}^{-1}$, $M_B = 111 \text{ g mol}^{-1}$

Substituting these values in the expression,

$$\Delta T_f = \frac{i \times K_f \times W_B \times 1000}{M_B \times W_A}, \text{ we get}$$

$$\Delta T_f = \frac{3 \times 1.86 \times 3 \times 1000}{111 \times 100} = 1.508 \text{ K}$$

Freezing point of solution,

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

$$= 273.15 \text{ K} - 1.508 \text{ K} = \mathbf{271.642 \text{ K}}$$

Q. 5. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated).

(Given: Molar mass of benzoic acid = 122 g mol^{-1} , K_f for benzene = $4.9 \text{ K kg mol}^{-1}$) [CBSE Delhi 2015]

Ans. The given quantities are

$W_B = 3.9 \text{ g}$, $W_A = 49 \text{ g}$, $\Delta T_f = 1.62 \text{ K}$, $M_B = 122 \text{ g mol}^{-1}$ and $K_f = 4.9 \text{ K kg mol}^{-1}$

Substituting these values in the equation,

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}, \text{ we get}$$

$$M_B = \frac{4.9 \times 3.9 \times 1000}{1.62 \times 49}$$

$$M_B = 240.74 \text{ g mol}^{-1}$$

Thus, observed molecular mass of benzoic acid in benzene = $240.74 \text{ g mol}^{-1}$

Normal molecular mass of benzoic acid = 122 g mol^{-1}

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

$$i = \frac{122 \text{ g mol}^{-1}}{240.74 \text{ g mol}^{-1}} = \mathbf{0.507}$$

As $i < 1$, therefore, benzoic acid will undergo association in benzene.

Q. 6. Calculate the mass of NaCl (molar mass = 58.5 g mol^{-1}) to be dissolved in 37.2 g of water to lower the freezing point by 2°C , assuming that NaCl undergoes complete dissociation.

(K_f for water = $1.86 \text{ K kg mol}^{-1}$)

[CBSE (F) 2015]

Ans. $\text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^-$, $i = \frac{2}{1} = 2$

Substituting $K_f = 1.86 \text{ K kg mol}^{-1}$, $W_A = 37.2 \text{ g}$, $M_B = 58.5 \text{ g mol}^{-1}$, $i = 2$, $\Delta T_f = 2^\circ\text{C}$ or 2 K in the equation,

$$W_B = \frac{\Delta T_f \times M_B \times W_A}{i \times K_f \times 1000}, \text{ we get}$$

$$W_B = \frac{2 \times 58.5 \times 37.2}{2 \times 1.86 \times 1000} = \mathbf{1.17 \text{ g}}$$

Q. 7. At 300 K, 30 g of glucose, $C_6H_{12}O_6$ present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of another glucose solution is 1.52 bar at the same temperature, calculate the concentration of the other solution. [CBSE 2019 (56/4/2)]

Ans.

$$\pi = \frac{W_B \times R \times T}{M_B \times V} = CRT$$

$$4.98 = \frac{30 \times R \times 300}{180 \times 1} = 50R \dots(i)$$

$$1.52 = C \times R \times 300 = 300CR \dots(ii)$$

Dividing equation (ii) by (i), we get

$$\frac{300CR}{50R} = \frac{1.52}{4.98} \Rightarrow C = 0.051 \text{ M}$$

Q. 8. A solution containing 1.9 g per 100 mL of KCl ($M = 74.5 \text{ g mol}^{-1}$) is isotonic with a solution containing 3 g per 100 mL of urea ($M = 60 \text{ g mol}^{-1}$). Calculate the degree of dissociation of KCl solution. Assume that both the solutions have same temperature. [CBSE 2019 (56/2/1)]

Ans. Isotonic solutions are those solutions which have the same osmotic pressure. If the osmotic pressures are equal at the same temperature, concentrations must also be equal. So,

For non-electrolyte Urea; $\pi = CRT$

For electrolyte KCl; $\pi = i CRT$

Thus, $C_{\text{urea}} RT = i C_{\text{KCl}} RT$

$$C_{\text{urea}} = i C_{\text{KCl}}$$

$$C_{\text{urea}} = \frac{3 \times 1000}{60 \times 100} = 0.5 \text{ M}$$

$$C_{\text{KCl}} = \frac{1.9 \times 1000}{74.5 \times 100} = 0.25 \text{ M}$$

So, $0.5 = i \times 0.25$

$$i = 2.0$$



$$0.25 \quad 0 \quad 0$$

$$0.25 - \alpha \quad \alpha \quad \alpha$$

Total moles after dissociation = $0.25 - \alpha + \alpha + \alpha$

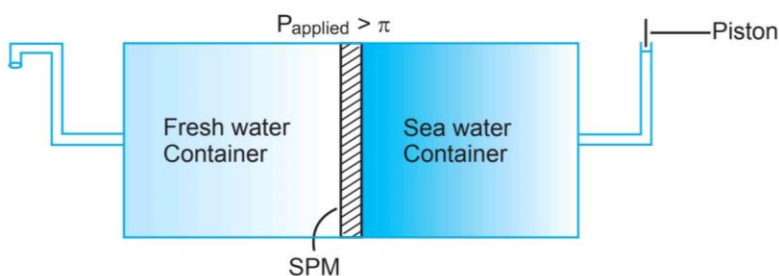
$$i = \frac{\text{Total number of moles after dissociation}}{\text{Total number of moles before dissociation}}$$

$$i = \frac{0.25 + \alpha}{0.25} \Rightarrow 2.0 = \frac{0.25 + \alpha}{0.25}$$

$$\alpha = 0.25 \text{ or } \alpha = 25\%$$

Q. 9. Given alongside is the sketch of a plant for carrying out a process.

- Name the process occurring in the given plant.
- To which container does the net flow of solvent take place?
- Name one SPM which can be used in this plant.
- Give one practical use of the plant.



- Ans.**
- Reverse osmosis.
 - Fresh water container.
 - Cellulose acetate placed on a suitable support.
 - Desalination of sea water.

Long Answer Questions

[5 marks]

Q. 1. (i) Define the following terms:

(a) Molarity

(b) Molal elevation constant (K_b)

(ii) A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution.

[CBSE (AI) 2014]

Ans. (i) (a) Molarity may be defined as number of moles of solute dissolved in one litre of solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in litre)}}$$

(b) Molal elevation constant may be defined as the elevation in boiling point when one mole of solute is dissolved in 1000 grams of the solvent.

(ii) Osmotic pressure, $\pi = \frac{W_B \times R \times T}{M_B \times V}$

$$\text{Osmotic pressure of urea solution} = \frac{15 \times R \times T}{60 \times 1}$$

$$\text{Osmotic pressure of glucose solution} = \frac{W_B \times R \times T}{180 \times 1}$$

As, Osmotic pressure of urea solution = Osmotic pressure of glucose solution

$$\text{Therefore, } \frac{15 \times R \times T}{60 \times 1} = \frac{W_B \times R \times T}{180 \times 1}$$

$$\text{Mass of glucose, } W_B = \frac{15 \times 180}{60} = 45 \text{ g}$$

Q. 2. (i) Explain why on addition of 1 mol glucose to 1 litre water the boiling point of water increases.

(ii) Henry's law constant for CO_2 in water is $1.67 \times 10^8 \text{ Pa}$ at 298 K. Calculate the number of moles of CO_2 in 500 ml of soda water when packed under $2.53 \times 10^5 \text{ Pa}$ at the same temperature.

[CBSE (AI) 2017C]

Ans. (i) On addition of glucose, a non-volatile solute to water (a volatile solvent) the vapour pressure of water decreases. In order to make the solution boil, its vapour pressure must be increased by raising the temperature above the boiling point of pure water. In other words, there is an increase in the boiling point of water.

(ii) According to Henry's law, $p_{\text{CO}_2} = K_H \times x_{\text{CO}_2}$ or $x_{\text{CO}_2} = \frac{p_{\text{CO}_2}}{K_H}$

$$\therefore x_{\text{CO}_2} = \frac{2.53 \times 10^5 \text{ Pa}}{1.67 \times 10^8 \text{ Pa}} = 1.51 \times 10^{-3}$$

Mass of water = Density of water \times volume of water

$$= 1 \text{ g mL}^{-1} \times 500 \text{ mL} = 500 \text{ g}$$

$$\text{Moles of water, } n = \frac{\text{Mass of water}}{\text{Molar mass}} = \frac{500 \text{ g}}{18 \text{ g mol}^{-1}} = 27.78 \text{ mol}$$

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}} + n_{\text{CO}_2}} = \frac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}}} \text{ or } n_{\text{CO}_2} = x_{\text{CO}_2} \times n_{\text{H}_2\text{O}}$$

$$n_{\text{CO}_2} = 1.51 \times 10^{-3} \times 27.78 \text{ mol} \\ = 0.042 \text{ mol}$$

Q. 3. (i) Define the following terms:

- (a) Azeotrope (b) Osmotic pressure
(c) Colligative properties

(ii) Calculate the molarity of 9.8% (w/w) solution of H_2SO_4 if the density of the solution is 1.02 g mL^{-1} . (Molar mass of $H_2SO_4 = 98 \text{ g mol}^{-1}$) [CBSE (F) 2014]

- Ans.** (i) (a) The binary mixtures of liquids having same composition in liquid and vapour phase and boil at a constant temperature are called azeotropes.
(b) The excess of pressure which must be applied to the solution side to prevent the passage of solvent into it through a semipermeable membrane is called osmotic pressure.
(c) The properties of solutions which depend only on the number of solute particles in the solution but independent of their nature are called colligative properties.
(ii) Let the mass of solution = 100 g
 \therefore Mass of $H_2SO_4 = 9.8 \text{ g}$

$$\text{Number of mole of } H_2SO_4 = \frac{\text{Mass of } H_2SO_4}{\text{Molar Mass}} = \frac{9.8 \text{ g}}{98 \text{ g mol}^{-1}} = 0.1 \text{ mol}$$

$$\begin{aligned} \text{Volume of solution} &= \frac{\text{Mass of solution}}{\text{Density of solution}} = \frac{100 \text{ g}}{1.02 \text{ g mL}^{-1}} = \frac{100}{1.02} \text{ mL} \\ &= \frac{100}{1.02} \text{ mL} \times \frac{1}{1000 \text{ mL L}^{-1}} = \frac{1}{10.2} \text{ L} \end{aligned}$$

$$\begin{aligned} \text{Molarity} &= \frac{\text{Moles of solute}}{\text{Volume of solution (in L)}} \\ &= \frac{0.1 \text{ mol}}{\frac{1 \text{ L}}{10.2}} = 1.02 \text{ mol L}^{-1} \text{ or } 1.02 \text{ M} \end{aligned}$$

Q. 4. Discuss biological and industrial importance of osmosis.

Ans. The process of osmosis is of great biological and industrial importance as is evident from the following examples:

- (i) Movement of water from soil into plant roots and subsequently into upper portion of the plant occurs partly due to osmosis.
(ii) Preservation of meat against bacterial action by adding salt.
(iii) Preservation of fruits against bacterial action by adding sugar. Bacterium in canned fruit loses water through the process of osmosis, shrivels and dies.
(iv) Reverse osmosis is used for desalination of water.

Q. 5. (i) When 2.56 g of sulphur was dissolved in 100 g of CS_2 , the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S_x).

[K_f for $CS_2 = 3.83 \text{ K kg mol}^{-1}$, Atomic mass of Sulphur = 32 g mol^{-1}]

- (ii) Blood cells are isotonic with 0.9 % sodium chloride solution. What happens if we place blood cells in a solution containing**
(a) 1.2% sodium chloride solution?
(b) 0.4% sodium chloride solution?

[CBSE Delhi 2016]

Ans. (i) Here, $W_B = 2.56 \text{ g}$, $W_A = 100 \text{ g}$, $\Delta T_f = 0.383 \text{ K}$, $K_f = 3.83 \text{ K kg mol}^{-1}$
Substituting these values in the expression, we get

$$\begin{aligned} M_B &= \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A} \\ M_B &= \frac{3.83 \times 2.56 \times 1000}{100 \times 0.383} = 256 \text{ g mol}^{-1} \end{aligned}$$

Now, molecular mass of $S_x = x \times 32 = 256$

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

Therefore, formula of sulphur = S_8

- (ii) (a) Water will flow out of the cell and they would shrink.
(b) Water will flow into the cell and they would swell.

Q. 6. (i) Why a person suffering from high blood pressure is advised to take minimum quantity of common salt?

(ii) 2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is $4.9 \text{ K kg mol}^{-1}$. What is the percentage association of acid if it forms dimer in solution? [CBSE 2019 (56/5/2)]

Ans. (i) Osmotic pressure is directly proportional to the concentration of the solutes. Our body fluid contains a number of solutes. On taking large amount of common salt, Na^+ and Cl^- ions enter into the body fluid thereby raising the concentration of the solutes. As a result, osmotic pressure increases which may rupture the blood cells.

(ii) The given quantities are

$$W_B = 2 \text{ g}, W_A = 25 \text{ g}, \Delta T_f = 1.62 \text{ K}, K_f = 4.9 \text{ K kg mol}^{-1}$$

Substituting these values in equation $M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$, we get

$$M_B = \frac{4.9 \times 2 \times 1000}{1.62 \times 25} = 241.98 \text{ g mol}^{-1}$$

Thus, observed molecular mass of benzoic acid in benzene = $241.98 \text{ g mol}^{-1}$

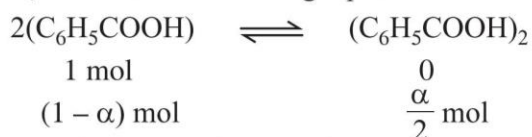
Normal molecular mass of $C_6H_5COOH = 122 \text{ g mol}^{-1}$

$$\therefore i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} = \frac{122 \text{ g mol}^{-1}}{241.98 \text{ g mol}^{-1}} = 0.504$$

$$i = 0.504 \quad \dots(i)$$

If α represents the degree of association of solute then we would have $(1 - \alpha)$ mole of benzoic acid left in unassociated form and corresponding $\frac{\alpha}{2}$ as associated moles of benzoic acid at equilibrium.

Now, consider the following equilibrium for the acid:



Thus, total number of moles of particles at equilibrium

$$= 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

$$i = \frac{\text{Total number of moles of particles after association}}{\text{Number of moles of particles before association}}$$

$$i = \frac{1 - \frac{\alpha}{2}}{1} = 1 - \frac{\alpha}{2} \quad \dots(ii)$$

From (i) and (ii), we have

$$0.504 = 1 - \frac{\alpha}{2}$$

$$\frac{\alpha}{2} = 1 - 0.504 = 0.496$$

$$\text{or } \alpha = 0.496 \times 2 = \mathbf{0.992}$$

Therefore, degree of association of benzoic acid in benzene is **99.2%**.

Q. 7. (i) Give reasons for the following:

(a) At higher altitudes, people suffer from a disease called anoxia. In this disease, they become weak and cannot think clearly. [CBSE 2019 (56/4/1)]

(b) When mercuric iodide is added to an aqueous solution of KI, the freezing point is raised.

(ii) 0.6 mL of acetic acid (CH_3COOH), having density 1.06 g mL^{-1} , is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C . Calculate the van't Hoff factor and the dissociation constant of acid.

Ans. (i) (a) At higher altitudes, partial pressure of oxygen is less than that at ground level, so that oxygen concentration becomes less in blood or tissues. Hence, people suffer from anoxia.
(b) Due to the formation of complex $\text{K}_2[\text{HgI}_4]$, number of particles in the solution decreases and hence the freezing point is raised.

(ii) Mass = Density \times Volume

$$\therefore \text{Mass of acetic acid} = 1.06 \text{ g mL}^{-1} \times 0.6 \text{ mL} = 0.636 \text{ g}$$

$$\text{Number of moles of acetic acid} = \frac{\text{Mass of acetic acid}}{\text{Molar mass}} = \frac{0.636 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0106 \text{ mol}$$

$$\text{Mass of water} = 1 \text{ g mL}^{-1} \times 1000 \text{ mL} = 1000 \text{ g}$$

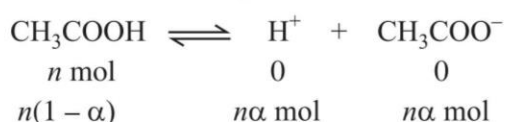
$$\begin{aligned} \text{Molality} &= \frac{\text{Number of moles of acetic acid}}{\text{Mass of water in grams}} \times 1000 \\ &= \frac{0.0106}{1000} \times 1000 = 0.0106 \text{ mol kg}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta T_f &= K_f \cdot m \\ &= 1.86 \text{ K kg mol}^{-1} \times 0.0106 \text{ mol kg}^{-1} \\ &= 0.0197 \text{ K} \end{aligned}$$

$$\begin{aligned} \text{van't Hoff Factor (i)} &= \frac{\text{Observed freezing point}}{\text{Calculated freezing point}} = \frac{0.0205 \text{ K}}{0.0197 \text{ K}} \\ i &= \mathbf{1.041} \end{aligned}$$

...(i)

If α is the degree of dissociation of acetic acid, then we would have $n(1 - \alpha)$ moles of undissociated acid, $n\alpha$ moles of CH_3COO^- and $n\alpha$ moles of H^+ ions at equilibrium.



Thus, total moles of particles = $n - n\alpha + n\alpha + n\alpha = n(1 + \alpha)$

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

...(ii)

From (i) and (ii), we have

$$1.041 = 1 + \alpha \Rightarrow \alpha = 1.041 - 1 = 0.041$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{CH}_3\text{COO}^-] = n(1 - \alpha) = 0.0106 (1 - 0.041) = 0.0106 \times 0.959$$

$$[\text{H}^+] = n\alpha = 0.0106 \times 0.041$$

$$[\text{CH}_3\text{COOH}] = n\alpha = 0.0106 \times 0.041$$

$$\begin{aligned} \therefore K_a &= \frac{0.0106 \times 0.041 \times 0.0106 \times 0.041}{0.0106 \times 0.959} \\ &= \mathbf{1.86 \times 10^{-5}} \end{aligned}$$