

# Solutions

## [TOPIC 1] Types, Concentration Terms and Solubility of Solution

Solutions are homogeneous mixtures of two or more than two components. The substances forming the solution are called components of the solution. The component present in smaller amount is called **solute** and the other present in larger amount in which solute is dissolved, is called **solvent**. The solutions containing two components are binary solutions, e.g. salt solution.

### 1.1. Types of Solution

Depending upon the nature of solute and solvent, solutions are classified as:

**Gaseous solutions** (in which gas acts as solvent, e.g. mixture of  $O_2$  and  $N_2$ ), **liquid solutions** (in which liquid acts as solvent, e.g.  $O_2$  dissolved in water), **solid solutions** (in which solid acts as solvent or present in large amounts, e.g. alloys).

### Different Methods to Express the Concentration of Solution

The concentration of the solutions can be expressed as follows:

#### Molarity ( $M$ )

It is defined as the number of moles of solute dissolved in one litre (or one cubic decimetre) of the solution.

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute} \times 1000}{\text{Volume of solution (mL)}}$$

$$\left(\text{Moles of solute} = \frac{W_2}{M_2}, \text{ where } W_2 = \text{mass of solute (g)} \text{ and } M_2 = \text{molar mass of solute}\right)$$

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}}$$

Molarity is a function of temperature and changes with change in temperature because volume depends upon temperature.

## Molality ( $m$ )

It is defined as the number of moles of solute per kilogram of the solvent.

$$\text{Molality } (m) = \frac{\text{Number of moles of solute} \times 1000}{\text{Mass of solvent (g)}}$$

## Normality ( $N$ )

It is the number of gram equivalents of the solute dissolved in one litre of the solution.

$$\text{Normality } (N) = \frac{\text{Number of gram equivalents of solute} \times 1000}{\text{Volume of solution (mL)}}$$

$$\left( \text{Gram equivalents of solute} = \frac{W_2}{\text{Equivalent weight}} \text{ where, } W_2 = \text{mass of solute} \right.$$

$$\left. \text{and Equivalent weight} = \frac{\text{Molecular mass}}{\text{Valency}} \right)$$

## Mole Fraction ( $\chi$ )

It is the number of moles of one component to the total number of moles of all the components present in the solution. For a binary solution having solvent 1 and solute 2,

$$\text{Mole fraction of solute, } \chi_2 = \frac{n_2}{n_1 + n_2}$$

$$\text{Similarly, mole fraction of solvent, } \chi_1 = \frac{n_1}{n_1 + n_2}$$

$$\therefore \chi_1 + \chi_2 = 1$$

Mole fraction of solution containing 'i' number of components,

$$\chi_i = \frac{n_i}{n_1 + n_2 + n_3 + \dots + n_i} = \frac{n_i}{\Sigma n_i}$$

**NOTE** Mass %, ppm, molality and mole fraction do not change with change in temperature while molarity decreases with rise in temperature.

## Parts per million (ppm)

When a solute is present in trace quantities, the concentration is expressed in parts per million.

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

## Mass per cent (w/w)

The mass percentage of a component in a given solution is the mass of the component per 100 g of the solution.

$$\text{Mass per cent} = \frac{\text{Mass of component} \times 100}{\text{Total mass of the solution}}$$

## Volume per cent (V/V)

The volume percentage is the volume of the component per 100 parts by volume of the solution.

$$\text{Volume per cent} = \frac{\text{Volume of the component} \times 100}{\text{Total volume of the solution}}$$

## Mass by volume percentage (w/V)

Mass by volume percentage is the mass of solute dissolved in 100 mL of the solution.

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

## Relation between molarity and molality

$$\text{Molality } (m) = \frac{M \times 1000}{(1000 \times d) - (M \times M_2)}$$

where,  $M$  is the molarity and  $M_2$  is the molar mass of component 2 (generally solute) and  $d$  is the density of solution (in  $\text{g cm}^{-3}$ ).

**NOTE**  $M_1V_1 = M_2V_2$ , similarly,  $N_1V_1 = N_2V_2$  (for all cases like acids-bases, dilution, etc).

## 1.2 Solubility

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent (at a specified temperature). It depends on nature of solute, solvent, temperature and pressure. Depending on solubility, solution can be saturated or unsaturated.

### Saturated Solution

Saturated solution is the solution in which no more solute can be dissolved at the same temperature and pressure.

### Unsaturated Solution

An unsaturated solution is the one in which more solute can be dissolved at the same temperature.

**NOTE** On dissolving the solid solute in a solvent, its concentration increases, this is called dissolution. While when some solute particles in solution collide with the other solid solute particles and get separated out of the solution, this process is called crystallisation.

## Dynamic Equilibrium

Dynamic equilibrium is the condition when number of solute particles going into the solution

is equal to the solute particles separating out, i.e. dissolution and crystallisation occur at the same rate.



From Le-Chatelier's principle, if in a nearly saturated solution, the dissolution process is endothermic ( $\Delta_{\text{sol}}H > 0$ ), the solubility should increase with rise in temperature and if it is exothermic ( $\Delta_{\text{sol}}H < 0$ ), the solubility should decrease.

## 1.3 Henry's Law

- It states that, at a constant temperature, the solubility of a gas in liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

$$S \propto p \text{ or } p = K_H \cdot S$$

where,  $S$  = solubility of gas

$p$  = partial pressure of gas at equilibrium

$K_H$  = Henry's law constant

Unit of solubility is same as that of concentration.

- In other words, "the partial pressure of the gas in vapour phase ( $p$ ) is directly proportional to the mole fraction ( $\chi$ ) of the gas in the solution."

$$p \propto \chi \text{ or } p = K_H \cdot \chi$$

- If we draw a graph between partial pressure of the gas *versus* mole fraction of the gas in solution, we get straight line whose slope is given by  $K_H$ .
- Higher the value of  $K_H$  at a given pressure, the lower is the solubility of the gas in the liquid. Solubility of gases increases with increase of pressure.

## Applications of Henry's Law

- To increase the solubility of  $\text{CO}_2$  in soft drinks and soda water, the bottle is sealed under high pressure.
- To avoid bends and the toxic effects of high concentrations of  $\text{N}_2$  in the blood, the cylinders used by scuba divers are filled with air diluted with He.

# [TOPIC 2] Vapour Pressure of Liquid Solutions, Ideal and Non-ideal Solutions

## 2.1 Raoult's Law for Volatile Solute

This law 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. For component 1,  $p_1 \propto x_1$  or  $p_1 = p_1^\circ x_1$

Similarly, for component 2,  $p_2 = p_2^\circ x_2$ ;

$$p_{\text{total}} = p_1 + p_2 = p_1^\circ x_1 + p_2^\circ x_2;$$

$$p_{\text{total}} = (1 - x_2) p_1^\circ + x_2 p_2^\circ$$

$$p_{\text{total}} = p_1^\circ + (p_2^\circ - p_1^\circ) x_2 \text{ as } (x_1 + x_2 = 1)$$

where,  $p_1^\circ$  and  $p_2^\circ$  are the vapour pressures of pure component 1 and 2 respectively.

If  $y_1$  and  $y_2$  are the mole fractions of the component 1 and 2 respectively in vapour phase, then  $p_1 = y_1 \times p_{\text{total}}$ . Similarly,  $p_2 = y_2 \times p_{\text{total}}$ .

## Raoult's Law a Special Case of Henry's Law

In the solution of a gas in a liquid, if one of the component is so volatile that it exists as a gas, then we can say that **Raoult's law becomes a special case of Henry's law** in which  $K_H$  becomes equal to  $p^\circ$ .

## 2.2 Ideal and Non-ideal Solutions

If a non-volatile solute is added to a solvent, then the vapour pressure of the solution decreases. This is because in solution, the surface has both solute and solvent molecules there by the fraction of the surface covered by the solvent molecules gets reduced, thus reducing the vapour pressure. On this basis, solution can be classified as ideal or non-ideal.

### Ideal Solutions

Ideal solutions obey Raoult's law over entire range of concentration. For these solutions,  $\Delta_{\text{mix}}H = 0$  and  $\Delta_{\text{mix}}V = 0$ . In binary solutions, if  $A-B$  interactions are nearly equal to  $A-A$  or  $B-B$  interactions then it is an ideal solution. Solutions of  $n$ -hexane and  $n$ -heptane, bromoethane and chloroethane, benzene and toluene, etc., are nearly ideal in behaviour.

### Non-ideal Solutions

Non-ideal solutions do not obey Raoult's law over entire range of concentration.

For such solutions,

$$\Delta_{\text{mix}}H \neq 0 \text{ and } \Delta_{\text{mix}}V \neq 0$$

The vapour pressure is either higher (positive deviation from Raoult's law) or lower (negative deviation from Raoult's law) than that predicted by Raoult's law.

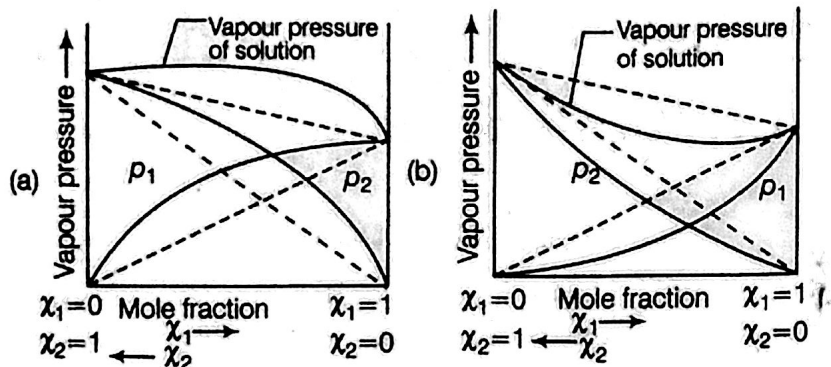
These are as follows:

### Positive Deviation and Negative Deviation

In case of positive deviation from Raoult's law

(e.g. mixture of ethanol and acetone, carbon disulphide and acetone),  $A-B$  (i.e. solute-solvent) interactions are weaker than those of  $A-A$  (solute-solute) or  $B-B$  (solvent-solvent) interactions, while in case of negative deviation from Raoult's law (e.g. mixture of phenol and aniline, chloroform and acetone),  $A-B$  interactions are stronger than those of  $A-A$  or  $B-B$  interactions.

The solutions showing **positive deviation** and **negative deviation** from Raoult's law are shown in fig. (a) and (b) respectively.



- (i) For positive deviation,  
 $\Delta H_{\text{mix}} = \text{Positive}$ ,  $\Delta V_{\text{mix}} = \text{Positive}$ .
- (ii) For negative deviation,  
 $\Delta H_{\text{mix}} = \text{Negative}$ ,  $\Delta V_{\text{mix}} = \text{Negative}$ .

## Azeotropes

The binary mixtures (solutions) that have the same composition in liquid and vapour phase and boil at constant temperature like a pure liquid are called **azeotropes** or **azeotropic mixtures**. The solutions which show large negative deviation from Raoult's law, form maximum-boiling azeotropes. e.g. Nitric acid-water mixture and the solutions which show large positive deviation from Raoult's law, form minimum boiling azeotropes. e.g. ethanol-water mixture.

# [TOPIC 3] Colligative Properties, and van't Hoff Factor

## 3.1 Colligative Properties

The properties of solutions which depend only on the number of solute particles, irrespective of their nature relative to the total number of particles present in solution are known as colligative properties.

Colligative properties  $\propto$  number of particles in the solution  $\propto \frac{1}{\text{Molar mass of solute}}$

Colligative properties are as follows:

### Relative Lowering of Vapour Pressure

When a non-volatile solute is dissolved in a solvent, vapour pressure of the solution becomes lower than that of the pure solvent which is

known as **lowering of vapour pressure**. The relative lowering of vapour pressure of a solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temperature. The expression for relative lowering of vapour pressure (**Raoult's law for non-volatile solute**) can be written as:

$$\frac{\Delta p_1}{p_1^\circ} = \frac{p_1^\circ - p_1}{p_1^\circ} = \chi_2$$

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1 + n_2} \quad \left( \text{Since, } \chi_2 = \frac{n_2}{n_1 + n_2} \right)$$

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1} \quad (\text{For dilute solutions, } n_2 \ll n_1)$$



$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

or

$$M_2 \text{ (solute)} = \frac{W_2 M_1}{W_1 \left( \frac{p_1^\circ - p_1}{p_1^\circ} \right)}$$

## Elevation in Boiling Point

The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure. The boiling point of a solution is always higher than the boiling point of the pure solvent in which the solution is prepared. This increase in boiling point is termed as **elevation in boiling point**.

If  $T_b^\circ$  is boiling point of pure solvent and  $T_b$  is the boiling point of solution, then the elevation in boiling point is represented as,

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

**Elevation in boiling point,**

$$\Delta T_b \propto m \text{ (where, } m \text{ is molality)}$$

or  $\Delta T_b = K_b m$  or  $\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1 \text{ (g)}}$

Also,

$$K_b = \frac{R \times M_1 \times (T_b^\circ)^2}{1000 \times \Delta_{\text{vap}} H}$$

where,  $K_b$  = boiling point elevation constant or molal elevation constant or ebullioscopic constant having unit  $\text{K kg mol}^{-1}$ .

## Depression in Freezing Point

The freezing point of a substance is that temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in solid phase. When a non-volatile solute is added to a solvent, the freezing point of the solution is always lower than that of pure solvent as the vapour pressure of the solvent decreases in the presence of non-volatile solute. This difference in freezing point is known as **depression of freezing point**, i.e.  $\Delta T_f = T_f^\circ - T_f$ .

where,  $T_f^\circ$  is the freezing point of pure solvent and  $T_f$  is the freezing point of solution.

**Depression of freezing point,**

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

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1 \text{ (g)}}$$

where,  $K_f$  = freezing point depression constant or molal depression constant or cryoscopic constant, having unit  $\text{K kg mol}^{-1}$

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1 \text{ (g)}}$$

Also,

$$K_f = \frac{R \times M_1 \times (T_f^\circ)^2}{1000 \times \Delta_{\text{fus}} H}$$

where,  $R$  and  $M_1$  are gas constant and molar mass of the solvent, respectively.  $T_f^\circ$  and  $T_b^\circ$  are freezing and boiling point of the pure solvent, respectively (in K).  $\Delta_{\text{fus}} H$  and  $\Delta_{\text{vap}} H$  are enthalpies for the fusion and vaporisation of the solvent, respectively.

## Osmosis and Osmotic Pressure

The process of flow of solvent molecules from solution of lower concentration to solution of higher concentration through semipermeable membrane is known as osmosis. The hydrostatic pressure which develops on account of osmosis is called **osmotic pressure** or the excess pressure that must be applied on the solution to prevent osmosis is called **osmotic pressure**.

Osmotic pressure ( $\pi$ ) is directly proportional to molarity ( $C$ ) of the solution at a given temperature  $T$ .

$$\pi \propto C$$

$$\pi = CRT \text{ or } \pi = \frac{n_2}{V} RT \quad \left( \text{where, } C = \frac{n_2}{V} \right)$$

or  $\pi V = \frac{W_2 RT}{M_2}$

or  $M_2 = \frac{W_2 RT}{\pi V}$

Osmotic pressure is used to determine molar masses of proteins, polymers and other macromolecules.

## Important Terminology Related to Osmosis

- (i) Two solutions having same osmotic pressure at a given temperature are called **isotonic solutions**.
- (ii) A solution having lower osmotic pressure than the other solution is called **hypotonic** while, the one with higher osmotic pressure is called **hypertonic**.
- (iii) **Reverse osmosis** If a pressure larger than the osmotic pressure is applied to the solution side, then the pure solvent flows out of the solution through the semipermeable membrane. This phenomenon is called reverse osmosis. It is used for the desalination of sea water.

**NOTE** People taking salty food, experience water retention in tissue cells and intercellular spaces due to osmosis. The resulting puffiness is called **edema**.

## Abnormal Molar Mass

For the substances undergoing association, dissociation, etc. in the solution, molecular mass determined from colligative properties is different (either lower or higher) from expected value.

This is known as abnormal molar mass. This change can be known by using van't Hoff factor.

## 3.2 van't Hoff Factor

It is the ratio of the experimental value of colligative property to the calculated value of the colligative property.

It is used to find out the extent of dissociation or association.

$$\text{van't Hoff factor, } i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

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

$$= \frac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$$

If  $i > 1$ , solute undergoes dissociation, and if  $i < 1$ , solute undergoes association.

- For association, when molecules of solute forms dimer,  $n = 2$ .

$$\text{Degree of association, } \alpha = \frac{i - 1}{\left(\frac{1}{n} - 1\right)}$$

where,  $n$  = number of particles associated.

- For dissociation of the solute  $AB$  type,  $m = 2$ , and for the solute  $AB_2$  or  $A_2B$  type ( $\text{CaCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ),  $m = 3$ .

Degree of dissociation,

$$\alpha = \frac{i - 1}{m - 1}$$

where,  $m$  = number of particles dissociated.

- Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:
  - (i) Relative lowering of vapour pressure of solvent,

$$\frac{p_1^\circ - p_1}{p_1^\circ} = i \frac{n_2}{n_1}$$

(ii) Elevation in boiling point,  $\Delta T_b = i K_b m$

(iii) Depression in freezing point,  $\Delta T_f = i K_f m$

(iv) Osmotic pressure of solution,

$$\pi = \frac{in_2}{V} RT$$