CHAPTER 02

Solutions

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

2. **Expression of concentration** Composition of a solution can be described by expressing its concentration.

   Several ways to describe the concentration of the solution quantitatively are as follows :

   - Percentage by mass (w/w)
   $$= \frac{\text{Mass of component in the solution}}{\text{Total mass of the solution}} \times 100$$
   - Percentage by volume (V/V)
   $$= \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100$$
   - Parts per million (ppm)
   $$= \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$
   - **Mole fraction** (χ) is the ratio of number of moles of one component to the total number of moles of all the components present in the solution.
   Mole fraction of solute,
   $$\chi_{(\text{solute})} = \frac{n_{(\text{solute})}}{n_{(\text{solute})} + n_{(\text{solvent})}}$$
   It is independent of temperature.

   For a given solution, sum of mole fractions of all the components of a solution is unity, i.e.
   $$\boxed{\chi_1 + \chi_2 + \ldots + \chi_i = 1}$$
   - **Molarity** (M) is defined as the number of moles of solute dissolved in one litre or one cubic decimetre of the solution.
   $$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in L)}}$$
   - **Normality** (N)
   $$= \frac{\text{Number of gram-equivalent of solute}}{\text{Volume of solution (in L)}}$$
   where,
   $$\text{g-equivalents} = \frac{\text{mass of solute } (W)}{\text{equivalent weight of solute } (E)}$$
   $$\text{Normality} \times \text{equivalent weight} = \text{Molarity} \times \text{molecular weight}$$
   - **Molality** (m) is defined as the number of moles of the solute per kilogram of the solvent.
   $$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

   (Molality, mole fraction, mass fraction, etc. are preferred over molarity, normality, etc. because they are temperature independent).

3. **Solubility** of a substance is its maximum amount that can be dissolved (in a specified amount of solvent) at a specified temperature. It depends upon the nature of solute and solvent at a specified temperature and pressure.

4. **Henry's law** states that, the partial pressure of the gas (p) is proportional to the mole fraction of the gas (χ) in the solution.

   Mathematically, it is expressed as
   $$p \propto \chi \quad \text{or} \quad p = K_H \chi$$
   where, K_H is called Henry's law constant.

   Higher the value of K_H at a particular temperature, lower is the solubility of the gas in the liquid.

   Solubility of gas decreases with increase in temperature. This is the reason that aquatic species are more comfortable in cold water rather than in warm water.

5. The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called **vapour pressure**.

6. **Raoult's law** states that at a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution, i.e. $p_1 \propto \chi_1$ and $p_1 = p_1^\circ \chi_1$.

   For a solution of two miscible components, 1 and 2,
   $p_{\text{total}} = p_1 + p_2 = p_1^\circ \chi_1 + p_2^\circ \chi_2$

   As we know, $\chi_1 + \chi_2 = 1$ or $\chi_1 = 1 - \chi_2$,
   $$p_{\text{total}} = p_1^\circ + (p_2^\circ - p_1^\circ)\chi_2$$

7. Solutions obeying Raoult's law over a entire range of concentration are called **ideal solutions** and those do not obey this law are called **non-ideal solutions**.

   For positive deviation,
   $A—B$ interaction $<$ $A—A$ or $B—B$ interactions
   e.g. CS_2 + acetone, acetone + benzene.

   For negative deviation,
   $A—B$ interaction $>$ $A—A$ or $B—B$ interactions
   e.g. chloroform + acetone, chloroform + benzene.

8. Azeotropes are binary mixtures having same composition in liquid and vapour phase and boil at constant temperature. There are two types of azeotropes which are:

   - **Minimum boiling azeotropes** These solutions show positive deviation from Raoult's law, e.g. ethanol-water mixture.
   - **Maximum boiling azeotropes** These solutions show large negative deviation from Raoult's law, e.g. nitric acid-water mixture.

9. The properties of solutions which depend only on the number of solute particles, not on the nature of the solute particles are known as **colligative properties**.

   These properties are as follows:

   - **Relative lowering of vapour pressure** in an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temperature.

$$\boxed{\chi_2 = \frac{\Delta p_1}{p_1^\circ} = \frac{p_1^\circ - p_1}{p_1^\circ}} \quad \text{or} \quad \boxed{\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{W_2 M_1}{W_1 M_2}}$$

Here, component number (1) is solvent and component number (2) is solute, W_1 and W_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute, respectively.

- **Elevation of boiling point** (ΔT_b) (Ebullioscopy) is the difference in the boiling points of the solution (T_b) and pure solvent (T_b°). It depends on the number of solute particles rather than on their nature.

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

Experimentally, $\Delta T_b \propto m$ or $\Delta T_b = K_b \cdot m$

$$\therefore \qquad \Delta T_b = K_b \times \frac{W_2 \times 1000}{M_2 \times W_1}$$

K_b = molal boiling point elevation constant or ebullioscopic constant (in K kg mol^{-1}).

- **Depression in freezing point** (ΔT_f) (Cryoscopy) is the decrease in the freezing point of solution when non-volatile solute is dissolve in it.

Thus, $\Delta T_f = T_f^\circ - T_f$

or $\Delta T_f = K_f \times m = K_f \times \dfrac{W_2 \times 1000}{M_2 \times W_1}$

where, m = molality and K_f= freezing point depression constant or cryoscopic constant (K kg mol^{-1}).

- **Osmosis** is a process which involves the flow of solvent molecules through a semipermeable membrane from pure solvent to the solution and **osmotic pressure** of the solution (π) is the pressure that just stops the flow of solvent.

$$\pi = CRT \quad \Rightarrow \quad \pi = \frac{W_2 RT}{VM_2} \quad (C = \text{Molarity})$$

10. **Isotonic solutions** are the solutions having same osmotic pressure at a given temperature. In case of two solutions of different osmotic pressures, the solution with higher osmotic pressure is called **hypertonic solution** and that with lower osmotic pressure is called **hypotonic solution.**

11. **Phenomena on the basis of osmosis** People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. This resulting puffiness or swelling is called **edema**.

12. In **reverse osmosis,** the solvent flows from solution side towards pure solvent, if external pressure is higher than osmotic pressure applied on solution side. It is used for desalination of sea water. Solvent moves from solution to pure solvent side.

13. Molar masses that are either lower or higher than the calculated (expected) or normal value are called **abnormal molar masses**.

14. **van't Hoff factor** (i) is defined as the ratio of the experimental or observed value of the colligative property to the calculated value of the colligative property.

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

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

In case of association/dissociation, i is also introduced in the formula of colligative properties. *These are as follows :*

i.e. $\Delta T_b = iK_b \cdot m$; $\Delta T_f = iK_f \cdot m$

$$\pi = iCRT \quad \text{and} \quad \frac{p_1^\circ - p_1}{p_1^\circ} = i\,\chi_{\text{solute}}$$

15. **Degree of Dissociation/Association** (α) **and van't Hoff Factor** (i)

α = degree of dissociation/association

- Degree of dissociation $\alpha = \dfrac{i-1}{n-1}$

  n = number of particles per molecules.

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

  $i = 1$, for non electrolytes; $i > 1$, for dissociation; $i < 1$, for association.

16. **Some Important Facts**

- Intramolecular H-bonding lowers boiling point.
- Benzoic acid and acetic acid dimerises in benzene.
- When egg is kept in saturated salt solution after removing the hard shell using dil. HCl, egg will shrink due to osmosis.
- $CaCl_2$ acts as a non-volatile solute and results depression in freezing point. Thus, snow is reduced (as it melts) and prevents blocking of roads in cold region.
- Ethylene glycol is mixed with radiator water to decrease the freezing point of water in cold region.
- Camphor is used for molecular mass determination due to its volatile nature.
- To increase the solubility of CO_2 in soft drinks, the bottle is sealed under high pressure.
- Helium-oxygen mixture is used by deep sea divers because of its low solubility in blood.