Chapter 2: Solutions

Prepared by
Shreemoyee Phukan
Silapathar College

Introduction

Solution is a homogeneous mixture of two or more substances. Binary solution has two components. Solute and solvent are the component of solution.

Types of Solutions

- **Aerosol** is solution of solid in gas or liquid in gas
- **Emulsion** is solution of liquid in liquid
- **Solid Solutions** are those solutions in which both the components of solution are solids. These are of two types:
    - **(i)** In **substitutional solid solutions** one element takes position of the other substance in the crystal lattice, e.g. bronze.
    - **(ii)** In **interstitial solid solutions,** second element enters into interstitial sites of the first element, e.g. tungsten carbide which is present in lesser quantity and solvent is present in larger proportion. All the three states of matter can act as solute or solvent.

S. No.	Solute	Solvent	Type/Name of solution	Examples
1.	Solid	Solid	Solid in Solid	Alloys, Amalgam
2.	Liquid	Solid	Liquid in Solid	Hydrated salts
3.	Gas	Solid	Gas in solid	Dissolved gases in mineral
4.	Solid	Liquid	Solid in liquid	Salt in water
5.	Liquid	Liquid	Liquid in liquid	Emulsion, Alcohol in water
6.	Gas	Liquid	Gas in liquid	Aerated drinks
7.	Solid	Gas	Solid in gas	Iodine vapour in air, adsorption of hydrogen over palladium
8.	Liquid	Gas	Liquid in gas	Mist, Humidity in air
9.	Gas	Gas	Gas in gas	Air

Solubility

Solubility of substance is defined as amount of solute dissolved in 100g of a solvent so as to form saturated solution at a given temperature.

- A solid dissolves in the solvent only when

    Hydration energy > lattice energy

    (Lattice energy is energy required to dissociate one mole of an ionic crystal into ions and hydration energy is the amount of energy released when 1 mole of ions are hydrated.)

    $$\Delta H_{(solution)} = \Delta H_{(lattice)} - \Delta H_{(hydration)}$$

- Larger the lattice energy of solute, smaller is the solubility.

- The solubility of ionic solids is higher in solvent having a high dielectric constant as compared to that having low dielectric constant.
- The solubility depends on temperature.
- All nitrates and acetates are soluble in water.

Henry's law

It states that solubility of a gas in liquid at a particular temperature is directly proportional to the pressure of gas above the liquid.

$$m \propto p \qquad \text{or} \qquad m = pK_H$$

(where, m = mass of the gas dissolved per unit volume of solvent, p = pressure of gas in equilibrium with solution at constant pressure, K_H = Henry's constant)

The most commonly used form of Henry's Law states that "The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (**x**) in the solution" i.e. **p = K$_H$ x**

- The value of Henry's constant depends on nature of gas, nature of solvent and temperature.
- The solubility of gas in liquid generally decreases with increase in temperature. As the temperature increases value of K_H increases and K_H is inversely proportional to solubility of a gas.
- Henry's law is used to determine the solubility of gases in liquid.

Different Units Used for Expressing Concentration of Solutions

(i) **Weight percentage:** It is the wt. of solute per 100g of solution (W/W) % by weight of solute

$$= \frac{\text{wt.of solute}}{\text{wt.of solution}} \times 100$$

(ii) **Volume percentage**

    (a) Wt. of solute/100 ml of solution (W/V)

    (b) Volume of solute/100 ml of solution (V/V)

(iii) **Part per million (ppm):** It is used to express the concentration of solutions in which solute is present in very small quantity.

Parts per million (ppm) of solute $= \dfrac{\text{mass of solute}}{\text{total mass of solute}} \times 10^6$

(iv) **Mole fraction (x)**

- Mole fraction of solute, A

$$(X_A) = \frac{\text{moles of solute}(n_A)}{\text{total moles in solution}(n_A + n_B)}$$

- Mole fraction of solvent, B

$$(X_B) = \frac{\text{moles of solvent}(n_B)}{\text{total moles in solution}(n_A + n_B)}$$

$$(X_1) = \frac{\text{moles of solvent }(n_1)}{\text{moles of solute }(n_2) + \text{moles of solvent }(n_1)} \text{ , similarly } X_2 = \frac{n_2}{n_1 + n_2}$$

(v) Molarity(M): Molarity of solution gives the number of moles of solute present in 1 L of the solution

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{volume of solution in L}}$$

Unit of molarity is mol L^{-1}. It is temperature dependent because volume changes with change in temperature.

(vi) Normality (N): Normality of solution gives the number of gram equivalents of solute present in 1 litre of the solution.

$$\text{Normality (N)} = \frac{\text{gram equivalent of solute}}{\text{volume of solution in L}}$$

- Gram equivalent of solute $= \dfrac{\text{mass of solute}}{\text{Eq. wt. of solute}}$

- Molarity and normality of solution are related as follows

$$\text{Normality} = \text{molarity} \times \frac{\text{molecular mass of solute}}{\text{equivalent mass of solute}}$$

(vii) Molality (m): Molality of solution gives the number of moles of solute present in 1000g (1 kg) of solution.

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

Unit of molality is mol kg^{-1}. It is temperature independent as mass does not change with change in temperature.

(viii) Formality (F): Formality of a solution is defined as the number of gram formula masses of solute dissolved per litre of solution.

$$\text{Formality (F)} = \frac{\text{no. of gram formula masses of solute}}{\text{volume of solution in litres}}$$

- Molality and mole fraction are preferred to express concentration of solution because they do not involve volume terms.

Some Useful Relationship Between Various Concentration Terms

(i) $x_2 = \dfrac{mM_1}{1+mM_1}$

(ii) $m = \dfrac{M}{1000d - M_1M_2} \times 100$

(iii) $x_2 = \dfrac{MM_1}{M(M_1 - M_2) + d}$

Where, M = molarity

d = density

x_2 = mole fraction of solute

M_1 = molecular mass of solvent

M_2 = molecular mass of solute

m = molality

Vapour Pressure

It is pressure exerted by vapour in equilibrium with liquid at a given temperature.

Vapour pressure $\propto \dfrac{1}{\text{forces of attraction between molecules}}$

- Vapour pressure depends on nature of liquid, temperature and purity of liquid.
- Vapour pressure of pure liquid is always more than its solution.
- Liquids having weak intermolecular forces are highly volatile, have high vapour pressure and evaporate easily.
- Vapour pressure of pure solvent decreases when non volatile solute is added to it.

Raoult's law

At any given temperature the partial vapour pressure of any component of a solution is equal to its mole fraction multiplied by the vapour pressure of this component in the pure state.

(i) **Raoult's law for non volatile solute:** At any given temperature the partial vapour pressure (P_1) of any component of a solution is equal to its mole fraction (X_1) multiplied by the vapour pressure of this component in the pure state (P_1^0).
$$P_1 = P_1^0 X_1$$

(ii) **Raoult's law for volatile solutes:** For solution having two components A and B
$$P_{total} = P_1 + P_2$$
$$= P_1^0 X_1 + P_2^0 X_2$$
$$= (P_2^0 - P_1^0)X_2 + P_1^0$$

Limitations of Raoult's law: It is applicable to very dilute solutions only.

Ideal Solutions and Non Ideal Solutions

(i) **Ideal solutions** are those solutions which obey Raoult's law at all concentrations and temperatures and during their formation no change in enthalpy and volume ($\Delta H_{(mixing)} = 0$ and $\Delta V_{(mixing)} = 0$) takes place are called ideal solutions.

Non ideal solutions are those solutions which do not follow Raoult's law at all concentrations and temperature, are called non ideal solutions.

S.No	Ideal Solution	Non-Ideal Solution
1.	They follow Raoult's law at all temperature and pressure.	They do not follow Raoult's law at all temperature and pressure.
2.	$\Delta V_{mixing} = 0$	$\Delta V_{mixing} \neq 0$
3.	$\Delta H_{mixing} = 0$	$\Delta H_{mixing} \neq 0$
4.	e.g. solution of hexane and heptane,$C_2H_5Br + C_2H_5Cl$	e.g.solution of water + C_2H_5OH,HNO_3 + water.

Types of Non Ideal Solutions

Non ideal solutions are of two types. Non ideal solution showing the positive deviation and non ideal solution showing negative deviations.

S.No	Non ideal solution showing positive deviation	Non ideal solution showing negative deviation
1.	Partial vapour pressure of each component of solution is greater than as expected from Raoult's law $$P_1 > P_1^0, P_2 > P_2^0$$ $$P_T > P_1^0 X_1 + P_2^0 X_2$$	Partial vapour pressure of each component of solution is less than as expected from Raoult's law $$P_1 < P_1^0, P_2 < P_2^0$$ $$P_T < P_1^0 X_1 + P_2^0 X_2$$
2.	ΔH_{mix} and ΔV_{mix} are positive.	ΔH_{mix} and ΔV_{mix} are negative.
3.	New interactions are weaker than those existing in pure components.	New interactions are stronger than those existing in pure components.
4.	e.g. Solution of $CH_3COCH_3 + C_2H_5OH$, and H_2O, C_2H_5OH, $CCl_4 + C_6H_5CH_3$, $CCl_4 + C_6H_6$, $CCl_4 + CHCl_3$	e.g. Solution of $H_2SO_4 + H_2O$ and $CH_3COCH_3 + CHCL_3$, $H_2O + HCl$, $CHCl_3 + C_6H_6$, $CHCl_3 + C_2H_5OC_2H_5$, $CH_3COCH_3 + C_6H_5NH_2$, $HNO_3 + H_2O$, $CH_3COOH + C_5H_5N$.

Azeotropic mixture (Or constant boiling mixtures) are mixtures of two liquids which boil at constant temperature and are distilled without changing composition. Non ideal solutions form azeotropico. These are of two types minimum boiling azeotropes and maximum boiling azeotropes.

S. No.	Properties	Minimum Boiling Azeotropes.	Maximum Boiling Azeotropes.
1.	Boiling point	Their boiling point is less than the boiling point of either of two pure components.	Their boiling point is more than the boiling point of either of two pure components.
2.	Composition	Non ideal solution showing positive deviation.	Non ideal solution showing negative deviation.
3.	e.g.	Solution of 95.5% H_2O+4.5%C_2H_5OH boils at 351.15 K.	Solution of 68% HNO_3 + 32% H_2O boils at 393.5 K.

Colligative properties

These are the properties of solution which depends only on the number of solute particles and do not depend on the nature of the solute particles. These are:

      (i)   Relative lowering in vapour pressure.
      (ii) Elevation in boiling point.
      (iii) Depression in freezing point.
      (iv) Osmotic pressure.

Relative Lowering in Vapour Pressure

    (i)   When a non-volatile solute is added to a solvent the vapour pressure is lowered due to percentage decrease (because now some solute particles occupy the surface) in surface area occupied by solvent. It results in decrease in rate of evaporation and vapour pressure.

    (ii) Relative lowering in vapour pressure is the ratio of lowering of vapour pressure to the vapour pressure of pure solvent. The solution containing non-volatile solute is equal to mole fraction of solute in the solution.

$$\frac{P_1^{\,0} - P_1^{\,S}}{P_1^{\,0}} = X_2 = \frac{n_2}{n_1 + n_2}$$

For dilute solution $\dfrac{P_1^{\,0}-P_1^{\,S}}{P_1^{\,0}} = \dfrac{X_2}{X_1} = \dfrac{w_2/M_2}{w_1/M_1} = \dfrac{W_2}{W_1}\dfrac{M_1}{M_2}$

Where, $\dfrac{P_1^{\,0}-P_1^{\,S}}{P_1^{\,0}}$ = relative lowering of vapour pressure.

X_2 = mole fraction of solute.

$P_1^{\,0}$ = vapour pressure of pure solvent.

$P_1^{\,S}$ = vapour pressure of solution.

Elevation in Boiling Point (Ebullioscopy)

(i) Boiling point is the temperature at which vapour pressure becomes equal to atmospheric pressure.

(ii) When non-volatile solute is added, it lowers the vapour pressure of the solvent therefore it must heated to higher temperature to make its vapour pressure equal to atmospheric in order to boil it. Therefore the solution boils at a higher temperature when solute is added to it.

$\Delta T_b = T_b - T^0$

Where, ΔT_b = elevation in boiling point.

$\qquad T_b$ = boiling point of solution.

$\qquad T^0$ = boiling point of pure solvent

$\qquad \triangle T_b = K_b \times m$

(iii) $\Delta T_b = \dfrac{K_b \times W_2 \times 1000}{M_2 \times W_1}$

K_b = molal elevation constant or Ebullioscopic constant.

W_2 = wt. of solute.

W_1 = wt. of solvent.

M_2 = molecular wt. of solute.

m = molality.

(iv) $K_b = \dfrac{RT_b^2}{1000 L_v}$

Where, L_v = latent heat of vaporisation. Molal elevation constant or Ebullioscopic constant (K_b) is defined as the elevation in boiling point produced when 1 mole of solute is dissolved in 1 kg solvent. The units of Ebullioscopic constant are K molality^{-1} or Kmol^{-1} kg.

(v) **Clausius Claperyon equation** is used to calculate the boiling point of solution at a given temperature when boiling point at some other pressure is given.

$$log\dfrac{P_2}{P_1} = \dfrac{\Delta H_v}{2.303\, R}\left[\dfrac{1}{T_1}-\dfrac{1}{T_2}\right]$$

Depression in Freezing Point (Cryoscopy)

(i) Freezing point is the temperature at which the liquid and solid state of same substance is in equilibrium and hence has same vapour pressure.

(ii) When non-volatile solute is added, it lowers the vapour pressure of the solvent therefore, the solid form separates at lower temperature. Therefore, the solution freezes at a lower temperature when solute is added to it.

$\Delta T_f = T^0 - T_f$

Where, ΔT_f = depression in freezing point.

T^0 = freezing point of pure solvent.

T_f = freezing point of solution.

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

(iv) $K_f = \frac{RT_f^2}{100L_f}$

Where, L_f = latent heat of fusion.

Molal depression constant or Cryoscopic constant (K_b) is defined as the depression in freezing point produced when 1 mole of solute is dissolved in 1 kg solvent. The units of cryoscopic constant are Kelvin kilogram per mole or Kkgmol^{-1}.

(v) Beckmann's thermometer is used to measure the elevation in boiling point and depression in freezing points. Their least count is 0.01°.

Osmosis

It is spontaneous movement of solvent particles from region of their lower concentration to higher concentration across semi permeable membrane.

Osmotic pressure

It is the minimum pressure which must be applied on the solution to prevent the entry of solvent into the solution through semi permeable membrane. It is measured by Berkeley and Hartley method.

S. No.	Isotonic Solution	Hypotonic Solution	Hypertonic Solution
1.	The solution have same osmotic pressure	The solution has lower osmotic pressure than other across semi permeable membrane.	The solution has higher osmotic pressure than other across semi permeable membrane.
2.	e.g. Human RBC and 0.9% NaCl	Human RBC and < 0.91% NaCl.	Human RBC and > 0.91% NaCl.
3.	The object is not effected.	The object swells and even bursts.	The object shrinks.

- In exosmosis, water flows out from cell into solution.
- In endosmosis, water flows inside cell from solution.
- Human RBC is isotonic with 0.91% NaCl solution.
- Osmotic pressure is the best Colligative property to determine the molecular mass of non-volatile solute and polymers.
- Plasmolysis is shrinking of living cell when placed in hypertonic solution.

Calculation of osmotic pressure (π)

$$\pi = \frac{n}{v}RT = CRT = \frac{wRT}{MV} \left(n = \frac{w}{M}\right)$$

For isotonic solution, $\pi_1 = \pi_2$

$$\therefore \qquad \frac{n_1}{v_2} = \frac{n_2}{v_2} \ or \ \frac{w_1}{M_1 V_1} = \frac{w_2}{M_2 V_2}$$

Reverse osmosis: When pressure applied on the solution is more than that its osmotic pressure, solvent flows from the solution into the pure solvent through semi-permeable membrane and Reverse osmosis takes place. Reverse osmosis is used for desalination of sea water (to get drinking water from it)

Abnormal Molecular Masses

These are observed in cases of solute which dissociate or associate when dissolved in water (or any other solvent).

van't Hoff factor: It is the ratio of two values i.e.

$$i = \frac{\text{observed value of colligative property}}{\text{normal vallue of colligative property}}$$

$$\text{Molecular mass} \propto \frac{1}{\text{colligative property}}$$

$$\therefore \qquad i = \frac{\text{normal molecualr mass}(M_c)}{\text{observed molecular mass}(M_o)}$$

For dissociation; $i > 1$ ($\because M_O < M_C$)
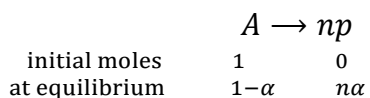
For association; $i < 1$ ($\because M_O > M_C$)

(i) **Modified formula for substances which associate or dissociate**
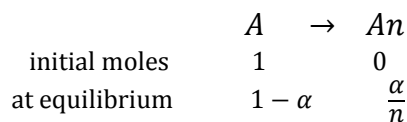$$\pi = iCRT$$
$$K_b = i\Delta T_b m$$
$$K_b = i\Delta T_f m$$

(ii) **van't Hoff factor and degree of dissociation**
$$A \longrightarrow np$$

initial moles	1	0
at equilibrium	$1-\alpha$	$n\alpha$

Total moles at equilibrium $= 1 - \alpha + n\alpha$

$$\therefore \qquad i = \frac{1 - \alpha + n\alpha}{1} \ \text{or} \ \alpha = \frac{i-1}{n-1}$$

(iii) **van't Hoff factor and degree of association**
$$A \quad \rightarrow \quad An$$

initial moles	1	0
at equilibrium	$1-\alpha$	$\frac{\alpha}{n}$

Total moles at equilibrium $= 1 - \alpha + \frac{\alpha}{n}$

$$i = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$$

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

$i < 1$,in case of association

$i > 1$,in case of dissociation

$i = 1$,when no association or dissociation takes place.

Comparison of osmotic pressure, freezing point, boiling point etc of solutions of non-electrolyte and different electrolytes:

In case of non-electrolytes (glucose, sugar, urea etc) the value of colligative property depends directly on the concentration. If the substance is an electrolyte ($NaCl$, $BaCl_2$ etc) it dissociates to give two or more ions then thae value of the colligative property depends upon the concentration of ions.

(e.g 0.1 M NaCl = 0.2M ions; 0.1 M $BaCl_2$ = 0.3 M ions)

Association : When benzoic acid is dissolved in benzene it undergoes association. Two moles of benzoic acid dimerize to give a new dinner of benzoic acid.
$$2(C_6H_5COOH) \ \rightleftharpoons \ (C_6H_5COOH)_2$$
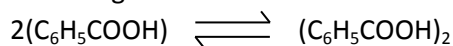
The molar mass comes out to be 244 which is the double of the normal molar mass 122 since the number of particles have been halved due to association. When *i<1,association* takes place and the theoretical molar mass is less than that calculated from colligative property.
Dissociation: When the particles in solution are more than the dissolve number of solute particles, the solute is said to have undergone dissociation. For example, NaCl is an electrolyte. It undergoes dissociation to produce Na^+ and Cl^- ions. Some NaCl may remain in undissociated form also.

$$NaCl \ \rightleftharpoons \ Na^+ + Cl^-$$
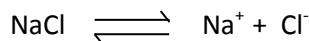
When $i > 1$, dissociation occurs and the theoretical molar mass is more than the calculated colligative property.
Degree of dissociation: It is denoted by α. It is the ratio of number of molecules dissociated to the total number of molecules.