Chapter 2: Solutions

Solution is a homogeneous mixture of two or more substances in same or different physical phases. The substances forming the solution are called components of the solution. On the basis of number of components a solution of two components is called binary solution.

Solute and Solvent

In a binary solution, solvent is the component which is present in large quantity while the other component is known as solute.

Classification of Solutions

(A) Following types of solutions are seen on the basis of physical state of solute and solvent.

S.No.	Solute	Solvent	Examples
Solid solutions			
1	Solid	Solid	Alloys
2.	Liquid	Solid	Hydrated salts, Amalgam of Hg with Na
3.	Gas	Solid	Dissolved gases in mineral
Liquid solutions			

the temperature. Thus, aquatic species are more comfortable in cold water [more dissolved O_2] rather than Warm water.

Applications

1. In manufacture of soft drinks and soda water, CO_2 is passed at high pressure to increase its solubility.

2. To minimise the painful effects (bends) accompanying the decompression of deep sea divers. O_2 diluted with less soluble. He gas is used as breathing gas.

3. At high altitudes, the partial pressure of O_2 is less then that at the ground level. This leads to low concentrations of O_2 in the blood of climbers which causes „anoxia".

Concentration of Solutions

The concentration of a solution is defined as the relative amount of solute present in a solution. On the basis of concentration of solution there are two types of solutions.

(i) Dilute solution

(ii) Concentrated solution

Methods of Expressing Concentration of Solutions

Various expression for the concentrations of solutions can be summarised as

(i) Percentage by weight

(w / w %) It is defined as the amount of solute present in 100 g of solution.

w / w % = weight of solute / weight of solution * 100

Normality = number of grams – equivalent of solute / volume of solution in L

Number of gram-equivalents of solute = mass of solute in gram / equivalent weight

[Relationship between normality and molarity N x Eq. weight = M x mol. weight]

If two solutions of the same solute having volumes and molarities V_1, M_1 and V_2, M_2 are mixed, the molarity of the resulting solution is

$$M = \frac{V_1M_1 + V_2M_2}{V_1 + V_2}$$

$$\text{Similarly, Normality } (N) = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

To dilute V_1 mL of a solution having molarity M_1 to molarity M_2 up to the final volume V_2 mL, the volume of water added is

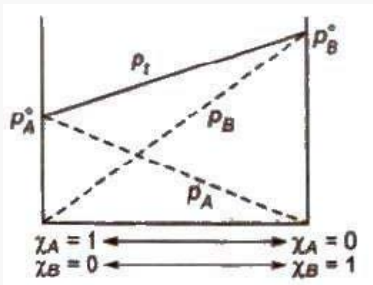$$V_2 - V_1 = \left(\frac{M_1 - M_2}{M_2}\right)V_1.$$

$$\text{Similarly, } V_2 - V_1 = \left(\frac{N_1 - N_2}{N_2}\right)V_1$$

(viii) Formality (F) It is the number of formula weights of solute present per litre of the solution.

Formality = moles of substance added to solution / volume of solution (in L))

(ix) Mass fraction Mass fraction of any component in the solution is the mass of that component

conditions :

(i) Solution must obey Raoult"s law, i.e.,

$$P_A = P_A^\circ \chi_A, \; P_B = P_B^\circ \chi_B$$

(ii) $\Delta H_{mix} = 0$ (No energy evolved or absorbed)

(iii) $\Delta V_{mix} = 0$ (No expansion or contraction on mixing)

Some solutions behave like nearly ideal solutions, e.g., benzene + toluene. n-hexane + nheptane, ethyl iodide + ethyl bromide, chlorobenzene + bromobenzene.
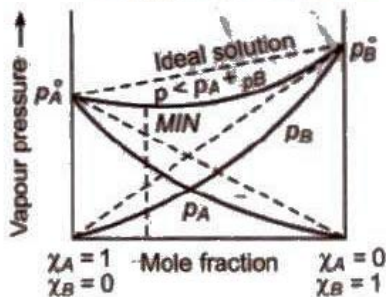
Non-ideal Solutions

Those solutions which shows deviation from Raoult"s law is called non-ideal solution.

For such solutions,

$\Delta H_{mix} \neq 0$

$P_{total} < P_A X_A + P_B X_B$

For such solutions,

$$\Delta H_{mix} < 0, \quad \Delta V_{mix} < 0$$

Non-ideal solution showing negative deviation

Examples : $CHCl_3 + CH_3COCH_3$, $CHCl_3 + C_6H_6$, $H_2O + HCl$, $H_2O + HNO_3$, methanol + acetic acid.

Azeotropic Mixture

A mixture of two liquids which boils at a particular temperature like a pure liquid and distils over in the same composition is known as constant boiling mixtures. These are formed by nonideal solutions.

(i) Minimum boiling azeotropes

Above expression is used to find the molecular weight of an unknown solute dissolved in a given solvent. Where, W_B and W_A = mass of Solute and solvent respectively. M_B and M_A = molecular weight of solute and solvent respectively.

Ostwald and Walker method is used to determine the relative lowering of vapour pressure.

Elevation in Boiling Point (ΔT_b)

Boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. As the vapour pressure of a solution containing a nonvolatile solute is lower than that of the pure solvent, it boiling point will be higher than that of the pure solvent as shown in figure. The increase in boiling point is known as elevation in boiling point, ΔT_b
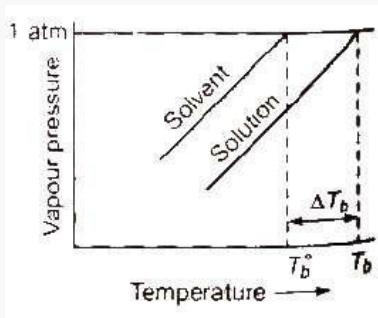
$\Delta T_b = T_b - T^\circ_b$ $\Delta T_b = K_b$ m (where; m = molality)

K_b is molal elevation constant or ebullioscopic constant. Molecular mass of solute can be calculated

where, K_f is molal depression constant or cryoscopic constant.

K_f has units of K / m or K kg mol^{-1}.

Ethylene glycol is usually added to water in the radiator to lower its freezing point. It is called antifreeze solution.

[Common salt (NaCI) and anhydrous CaC12 are used to clear snow on the roads because they depress the freezing point of water. The freezing point depression is determined by Beckmann method or Rast method.]

Calculations of molal elevation constant (K_b) and molal depression constant (K_f)

$$K_b = \frac{M_A R(T_b^{\circ})^2}{\Delta H_v}, \quad K_f = \frac{M_A \cdot R(T_f^{\circ})^2}{\Delta H_f}$$

T_b° = boiling point of solvent

T_f° = freezing point of solvent

ΔH_f = molar enthalpy of fusion

ΔH_n = molar enthalpy of vaporisation

Osmotic Pressure (π)

Osmosis is the phenomenon of spontaneous flow of the solvent molecules through a semipermeable membrane from pure solvent to solution or from a dilute solution to concentrated solution. It was

(ii) Hypotonic solution

A solution is called hypotonic if its osmotic pressure is lower than that of the solution from which it is separated by a semipermeable membrane.

(iii) Isotonic solution

Two solutions are called isotonic if they exert the same osmotic pressure. These solutions have same molar concentration. 0.91% solution of pure NaCl is isotonic with human RBC"s.

Two solutions are isotonic if they have the same molar concentration, e.g., if x % solution of X is isotonic with y % solution of Y, this means molar concentration of X = Molar concentration of Y

$$\frac{x}{100} \times \frac{1000}{M_X} = \frac{y \times 1000}{100 \times M_Y} \quad \Rightarrow \quad \frac{x}{M_X} = \frac{y}{M_Y}$$

Osmotic pressure method is the best method for determining the molecular masses of polymers since observed value of any other colligative property is too small to be measured with reasonable accuracy.

Reverse osmosis

When the external pressure applied on the solution is more than osmotic pressure, the solvent flows from the solution to the pure solvent, I which is called reverse osmosis. Desalination of sea water is done by reverse Osmosis.

Abnormal Molecular Masses

In some cases, observed colligative properties deviate from their normal calculated values due to association or dissociation of molecules. As we know,

$$\alpha = \frac{\quad}{n-1}$$

Degree of Association (α) and van't Hoff Factor (i)

If n molecules of a substance A associate to form An and α is the degree of association then

$$nA \longrightarrow A_n$$

Initially	1 mol	0
At equilibrium	$1-\alpha$	$\dfrac{\alpha}{n}$

Total number of moles at equilibrium

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

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

$$\Rightarrow \qquad \alpha = \frac{i-1}{\dfrac{1}{n} - 1}$$

van"t Hoff factor (i) > 1 for solutes undergoing dissociation and it is < 1 for solutes undergoing association.

- Solutions:
  Solutions are the homogeneous mixtures of two or more than two components.
- Binary solution:
  A solution having two components is called a binary solution.
- Components of a binary solution
  It includes solute and solvent.
    a) When the solvent is in solid state, solution is called solid solution.
    b) When the solvent is in liquid state, solution is called liquid solution.
    c) When the solvent is in gaseous state, solution is called gaseous solution.
- Concentration:
  It is the amount of solute in given amount of solution.
- Mass by volume percentage (w/v):
  Mass of the solute dissolved in 100 mL of solution.
- Molality (m) is the number of moles of solute present in 1kg of solvent.
$$Molality = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kilograms}}$$
- Molarity (M) is the number of moles of solute present in 1L of solution.
$$Molality = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}}$$
- Normality is the number of gram equivalent of solute dissolved per litre of solution.
$$Molality = \frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in litres}}$$
- Solubility:
  It is the maximum amount that can be dissolved in a specified amount of solvent at a specified temperature.
- Saturated solution:
  It is a solution in which no more solute can be dissolved at the same temperature and pressure.
- In a nearly saturated solution if dissolution process is an endothermic process, solubility increases with increase in temperature.
- In a nearly saturated solution if dissolution process is an exothermic process, solubility decreases with increase in temperature.
- Henry's Law:

It states "at a constant temperature the solubility of gas in a liquid is directly proportional to the pressure of gas". In other words, "the partial pressure of gas in vapour phase is proportional to the mole fraction of the gas in the solution".

$$P = K_H x$$

- When a non-volatile solute is dissolved in a volatile solvent, the vapour pressure of solution is less than that of pure solvent.
- Raoult's law:

  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".

  $$p_1 = p^0_1 X_1; p_2 = p^0_2 X_2$$

- Using Dalton's law of partial pressure the total pressure of solution is calculated.

  $$p_{total} = p^0_1 + (p_2 - p^0_1)X_2$$

- Comparison of Raoult' law and Henry's law:

  It is observed that the partial pressure of volatile component or gas is directly proportional to its mole fraction in solution. In case of Henry's Law the proportionality constant is K_H and it is different from p10 which is partial pressure of pure component. Raoult's Law becomes a special case of Henry's Law when K_H becomes equal to p10 in Henry's law.

- Classification of liquid –liquid solutions:

  It can be classified into ideal and non-ideal solutions on basis of Raoult's Law.

- Ideal solutions:
  a) The solutions that obey Raoult's Law over the entire range of concentrations are known as ideal solutions.
  b) $\Delta_{mix} H = 0$ and $\Delta_{mix} V = 0$
  c) The intermolecular attractive forces between solute molecules and solvent molecules are nearly equal to those present between solute and solvent molecules i.e. A-A and B-B interactions are nearly equal to those between A-B.

- Non-ideal solutions:
  a) When a solution does not obey Raoult's Law over the entire range of concentration, then it is called non-ideal solution.
  b) $\Delta_{mix} H \neq 0$ and $\Delta_{mix} V \neq 0$
  c) The intermolecular attractive forces between solute molecules and solvent molecules are not equal to those present between solute and solvent molecules i.e. A-A and B-B interactions are not equal to those between A-B

- Types of non- ideal solutions:

  There are two types of non-ideal solutions namely,
  a) Non ideal solution showing positive deviation
  b) Non ideal solution showing negative deviation

- Non ideal solution showing positive deviation
  a) The vapour pressure of a solution is higher than that predicted by Raoult's Law.

b) The intermolecular attractive forces between solute-solvent molecules are weaker than those between solute-solute and solvent-solvent molecules i.e., A-B < A-A and B-B interactions.

- Non ideal solution showing negative deviation
  a) The vapour pressure of a solution is lower than that predicted by Raoult's Law.
  b) The intermolecular attractive forces between solute-solvent molecules are stronger than those between solute-solute and solvent-solvent molecules i.e. A-B > A-A and B-B interactions.

- Azeotopes:
  These are binary mixtures having same composition in liquid and vapour phase and boil at constant temperature. Liquids forming azeotrope cannot be separated by fractional distillation.

- Types of azeotropes:
  There are two types of azeotropes namely,
  a) Minimum boiling azeotrope
  b) Maximum boiling azeotrope

- The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.

- The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition.

- Colligative properties:
  The properties of solution which depends on only the number of solute particles but not on the nature of solute are called colligative properties.

- Types of colligative properties:
  There are four colligative properties namely,
    a) Relative lowering of vapour pressure
    b) Elevation of boiling point
    c) Depression of freezing point
    d) Osmotic pressure

- Relative lowering of vapour pressure:
  The difference in the vapour pressure of pure solvent p_1^0 and solution p_1 represents lowering in vapour pressure $(p_1^0 - p_1)$.

- Relative lowering of vapour pressure:
  Dividing lowering in vapour pressure by vapour pressure of pure solvent is called relative lowering of vapour pressure $\left(\dfrac{p_1^0 - p_1}{p_1^0} \right)$

- Relative lowering of vapour pressure is directly proportional to mole fraction of solute. Hence it is a colligative property.

- Elevation of boiling point: $\left(\dfrac{p_1^0 - p_1}{p_1^0}\right) = X_2$

  The difference in boiling points of solution T_b and pure solvent T_b^0 is called elevation in boiling point $\Delta T = T_b - T_b^0$

- For a dilute solution elevation of boiling point is directly proportional to molal concentration of the solute in solution. Hence it is a colligative property.

$$\Delta T_b = \frac{k_b \text{ x } 1000 \text{ x } w_2}{M_2 \text{ x } w_1}$$

- Depression of freezing point:

  The lowering of vapour pressure of solution causes a lowering of freezing point compared to that of pure solvent. The difference in freezing point of the pure solvent T_f^0 and solution T_f is called the depression in freezing point.

$$\Delta T = T_f^0 - T_f$$

- For a dilute solution depression in freezing point is a colligative property because it is directly proportional to molal concentration of solute.

$$\Delta T_f = \frac{k_f \text{ x } 1000 \text{ x } w_2}{M_2 \text{ x } w_1}$$

- Osmosis:

  The phenomenon of flow of solvent molecules through a semi permeable membrane from pure solvent to solution is called osmosis.

- Osmotic pressure:

  The excess pressure that must be applied to solution to prevent the passage of solvent into solution through a semipermeable membrane is called osmotic pressure.

- Osmotic pressure is a colligative property as it depends on the number of solute particles and not on their identity.

- For a dilute solution, osmotic pressure (π) is directly proportional to the molarity (C) of the solution i.e. $\pi = CRT$

- Osmotic pressure can also be used to determine the molar mass of solute using the equation $M_2 = \dfrac{w_2 RT}{\pi V}$

- Isotonic solution:

  Two solutions having same osmotic pressure at a given temperature are called isotonic solution.

- Hypertonic solution:

  If a solution has more osmotic pressure than other solution it is called hypertonic solution.

- Hypotonic solution:

  If a solution has less osmotic pressure than other solution it is called hypotonic solution.

- Reverse osmosis:
  The process of movement of solvent through a semipermeable membrane from the solution to the pure solvent by applying excess pressure on the solution side is called reverse osmosis.
- Colligative properties help in calculation of molar mass of solutes.
- Abnormal molar mass:
  Molar mass that is either lower or higher than expected or normal molar mass is called as abnormal molar mass.
- Van't Hoff factor:
  Van't Hoff factor (i) accounts for the extent of dissociation or association.

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

$$= \frac{\text{Observed collogative property}}{\text{Calculated collogative property}}$$

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

- Value of i is less than unity in case solute undergo association and the value of i is greater than unity in case solute undergo dissociation.
- Inclusion of van't Hoff factor modifies the equations for colligative properties as:

$$\frac{p_1^0 - p_.}{p_1^0} = i.\frac{n_2}{n_1}$$

$$\Delta T_b = i.\frac{k_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$\Delta T_f = i.\frac{k_f \times 1000 \times w_2}{M_2 \times w_1}$$

$$\pi = i.\frac{n_2 RT}{V}$$