

SOLUTION

SOLUTION AND COLLIGATIVE PROPERTIES

Methods of expressing concentration of solution

Concentration of solution is the amount of solute dissolved in a known amount of the solvent or solution. The concentration of solution can be expressed in various ways as

(1) Percentage : It refers to the amount of the solute per 100 parts of the solution.

(i) Weight of weight percent

$$\% w / w = \frac{\text{Wt. of solute}}{\text{Wt. of solution}} \times 100$$

(ii) Weight of volume percent

$$\% w / v = \frac{\text{Wt. of solute}}{\text{Volume of solution}} \times 100$$

(iii) Volume to volume percent

$$\% v / v = \frac{\text{Vol. of solute}}{\text{Vol. of solution}} \times 100$$

(iv) Volume of weight percent

$$\% v / w = \frac{\text{Vol. of solute}}{\text{W. of solution}} \times 100$$

(2) Parts per million (ppm) and parts per billion (ppb) :

$$\text{ppm} = \frac{\text{mass of solute component}}{\text{Total mass of solution}} \times 10^6$$

$$\text{ppb} = \frac{\text{mass of solute component}}{\text{Total mass of solution}} \times 10^9$$

(3) Strength :

The strength of solution is defined as the amount of solute in grams present in one litre of the solution.

$$\text{Strength} = \frac{\text{Mass of solute in grams}}{\text{Volume of solution in litres}}$$

(4) Normality (N):

It is defined as the number of gram equivalent of a solute present per litre of the solution.

$$(i) \text{ Normality (N)} = \frac{\text{Number of g eq. of solute}}{\text{Volume of solution (l)}}$$

$$(ii) N = \frac{\text{Weight of solution in g}}{\text{g. eq. weight of solute} \times \text{Volume of solution (l)}}$$

$$(iii) N = \frac{\text{Strength of solution}}{\text{eq. wt. of solute}}$$

$$(iv) N = \frac{\text{Wt\%} \times \text{density} \times 10}{\text{Eq. wt.}}$$

(v) If volume V_1 and normally N_1 of solution is changed to new normality N_2 and volume V_2 then,
 $N_1 V_1 = N_2 V_2$ (Normality equation)

(vi) When two solutions of the same solute are mixed then normality of mixture (N) is

$$N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

(vii) When V_a ml of strong acid of normality N_a is mixed with V_b ml of strong base of normality N_b

(a) If $V_a N_a = V_b N_b$ (Solution will be neutral)

(b) If $V_a N_a < V_b N_b$ (Solution will be basic)

(c) If $V_a N_a > V_b N_b$ (Solution will be acidic)

5. Molarity (M): Molarity of a solution is the number of moles of the solute per litre of solution (or number of millimoles per ml. of solution).

Mathamatically molarity can be calculated by following formulas,

$$(i) \quad M = \frac{\text{No. of gram molecule of solute}}{\text{Vol. of solution in litres}}$$

$$(ii) \quad M = \frac{\text{Wt. of solute (in gm) per litre of solution}}{\text{Mol. wt. of solute}}$$

$$(iii) \quad M = \frac{\text{Wt. of solute (in gm)}}{\text{Mol. wt of solute}} \times \frac{1000}{\text{Vol. of solution in ml.}} \quad (iv) \quad M = \frac{10 \times \text{sp. gr. of the solution} \times \text{Wt. \% of the solute}}{\text{Mol. wt. of the solute}}$$

(v) If molarity and volume of solution are changed from (M_1, V_1) to (M_2, V_2) Then,

$$M_1 V_1 = M_2 V_2 \text{ (Molarity equation)}$$

Relation between molarity and normality

$$\text{Normality of solution} = \text{molarity} \times \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

$$\text{For an acid, } \frac{\text{Molecular mass}}{\text{Equivalent mass}} = \text{Basicity}$$

So, Normality of acid = molarity \times basicity

$$\text{For a base, } \frac{\text{Molecular mass}}{\text{Equivalent mass}} = \text{Acidity}$$

So, Normality of base = Molarity \times Acidity

6. Molality (m):

The number of molecule of gram molecules of the solute dissolved in 1000 g of the solvent said to be molality of solution.

$$(i) \quad m = \frac{\text{Number of moles of the solute}}{\text{Weight of the solvent in grams}} \times 1000$$

$$(ii) \quad m = \frac{\text{No. of gm moles of solute}}{\text{Wt. of solvent in kg}}$$

$$(iii) \quad m = \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}} \times \frac{1000}{\text{Wt. of solvent in g}}$$

6. Relation between molarity (M) and molality (m)

$$m = \frac{1000 \times M}{100 \times d - M \times m}$$

m = Molarity, d = Density of solution in gram/cc M_1 = molecular mass of solute.

7. Formality (F):

Formality of a solution is defined as the number of gram formula masses of the ionic solute dissolved in one litre

of the solution. Commonly, the term formality is used to express the concentration of the ionic solids which do not exist as molecules but exist as network of ions.

$$\text{Formality (F)} = \frac{\text{Mass of ionic solute (in gm)}}{(\text{gm. formula mass of solute}) \times (\text{Volume of solution (l)})}$$

8. Mole Fraction (X):

Mole fraction is defined as the ratio of number of moles of one component to the sum of number of moles of all the components (solvent and solute) present in the solution. It is denoted by the letter X.

$$\text{Mole fraction of A, } X_A = \frac{n_A}{n_A + n_B}$$

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

The sum of mole fractions of all the components in the solution is always one,

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

9. **Mass Fraction :** Mass fraction of a component in a solution is the mass of that component divided by the total mass of the solution. For a solution containing w_A gm of A and w_B gm of B

$$\text{Mass Fraction of A} = \frac{w_A}{w_A + w_B}, \quad \text{Mass Fraction of B} = \frac{w_B}{w_A + w_B}$$

10. **Demal unit (D):** One demal unit represents one mole of solute present in one litre of solution of 0°C.

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. These four well known colligative properties are:

- (1) Relative Lowering in vapour pressure.
- (2) Osmotic pressure of the solution
- (3) Elevation in boiling point of the solvent
- (4) Depression in freezing point of the solvent.

Lowering in 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.

- (1) **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.
- (2) **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.

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Rauolt's law :

When a non-volatile solute is dissolved in a volatile solvent then lowering in vapour pressure takes place.

“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.”

$$\frac{p^0 - p^s}{p^0} = \frac{n}{n + N} = X_{\text{solute}} \quad \dots(i) \quad \Rightarrow \quad \frac{p^0 - p^s}{p^s} = \frac{n}{N}$$

Azeotropic Mixture

The solutions which boil at constant temperature like a pure liquid and possess same composition in liquid as well as vapour state are called azeotropes as azeotropic mixture.

Azeotropes are also called constant boiling mixtures because whole of the azeotrope change into vapour state at constant temperature and their components cannot be separated by fractional distillation. Azeotropes are of two types as described below.

- (i) **Minimum boiling azeotropes:** These azeotropes are formed by those liquid pairs which show positive deviation from ideal behaviour. Such azeotropes have boiling points lower than either of the components.
- (ii) **Maximum boiling azeotropes:** These azeotropes are formed by those liquid pairs which show negative deviations from ideal behaviour. Such azeotropes have boiling points lower than either of the components.
- (1) **Osmosis:** The net spontaneous flow of solvent from pure solvent to solution or from solution of lower concentration into solution of higher concentration through a semi-permeable membrane is called Osmosis.

The minimum pressure required to stop the phenomenon of osmosis is called osmotic pressure (π).

$$\pi = i.C.S.T.$$

Osmosis may be divided in following types:

- (i) **Exo-Osmosis :** The outward osmotic flow of water from a cell containing an aqueous solution through a semi-permeable membrane is called as Exo-osmosis. For example, egg (after removing hard shell) placed in conc. NaCl solutions, will shrink due to exo-osmosis.
- (ii) **Endo-osmosis:** The inward flow of water into the cell containing an aqueous solution through a semi-permeable membrane is called as endo-osmosis. e.g. an egg placed in water swells up due to endo-osmosis.
- (iii) **Reverse osmosis:** If a pressure higher than osmotic pressure is applied on the solution or solution at higher concentration, then solvent will flow from the solution into the pure solvent or into solution at lower concentration through the semi-permeable membrane. Since here the flow of solvent is in the reverse direction to that observed in the usual osmosis, the process is called reverse osmosis.
- (i) **Measurement of osmotic pressure:** Following methods are used for the measurement of osmotic pressure, (a) Pfeffer's method (b) Morse and Frazer's method (c) Berkeley and Hartley's method (d) Townsend's reverse osmosis method (e) De Vries plasmolytic method.
- (ii) **Isotonic, Hypertonic and Hypotonic solutions**
 - (a) **Isotonic or Iso-osmotic solutions:** Two solutions of different substances having same osmotic pressure at same temperature are known as isotonic solution.

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

$$\left. \begin{array}{l} \text{Also,} \quad C_1 = C_2 \\ \text{or} \quad \frac{n_1}{V_1} = \frac{n_2}{V_2} \\ \text{or} \quad \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2} \end{array} \right\} \text{Secondary Conditions} \quad \dots(ii)$$

Eq. (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 (dissociation) are isotonic then, $\pi_1 = \pi_2$ but $C_1 \neq C_2$

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

- (b) Hypertonic and hypotonic solution: The solution which has more osmotic pressure than the other solution is said to be hypertonic solution and the solution which has lesser osmotic pressure than the other said to be hypotonic solution.

The flow of solvent is always from lower osmotic pressure to higher osmotic pressure i.e. from hypotonic to hypertonic solution.

Note : Osmosis pressure of mixture of solution -

(a) of same solute $\pi_1 v_1 + \pi_2 v_2 = \pi_R (v_1 + v_2)$

(b) of two different solutes, $\pi = \pi_1 + \pi_2 = \frac{(n_1 i_1 + i_2 n_2)}{(v_1 + v_2)} RT$

3. Elevation in b.pt of the solvent (Ebullioscopy)

Boiling point of a liquid is defined as the temperature at which its vapour pressure becomes equal to atmospheric pressure. $\Delta T_b = i \times K_b \times m$ where, $\Delta T_b = T_b^s - T_b^0$ and $K_b = \frac{RT_b^2}{1000l_v}$

4. Depression of f.pt. of the solvent (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 is defined as the temperature at which the liquid and the solid states of a substance have the same vapour pressure. $\Delta T_f = i \times K_f \times m$ where, $\Delta T_f = T_f^0 - T_f^s$ and $K_f = \frac{RT_f^2}{1000l_f}$

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 defined as

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} = \frac{\text{Observed value of colligative property}}{\text{Calculated value of that colligative property assuming no association or dissociation}} = \frac{\text{No. of particles after association or dissociation}}{\text{No. of particles before association or dissociation}}$$

Degree of dissociation (α): It is defined as the fraction of total molecules which dissociates into simpler molecules or ions. $\alpha = \frac{i-1}{m-1}$; m = number of particles obtained after 100% dissociation of 1 molecule of solute 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.

$$\alpha = \frac{1-i}{1-1/m}; m = \text{number of solute particles associate to form one giant particle in solution.}$$

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
1. Obey Raoult's Law at every range of concentration	1. Do not obey Raoult's law	1. Do not obey Raoult's law
2. $\Delta H_{\text{mix}} = 0$	2. $\Delta H_{\text{mix}} > 0$	2. $\Delta H_{\text{mix}} < 0$.
3. $\Delta V_{\text{mix}} = 0$	3. $\Delta V_{\text{mix}} > 0$,	3. $\Delta V_{\text{mix}} < 0$.
4. $P = P_A + P_B = P_A^0 X_A + P_B^0 X_B$	4. $P_A > P_A^0 X_A$; $P_B > P_B^0 X_B$	4. $P_A < P_A^0 X_A$; $P_B < P_B^0 X_B$
where $P_A = P_A^0 X_A$ & $P_B = P_B^0 X_B$	$\therefore (P_A + P_B) > (P_A^0 X_A + P_B^0 X_B)$	$\therefore (P_A + P_B) < (P_A^0 X_A + P_B^0 X_B)$
5. Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.	5. 'A' and 'B' escape easily showing higher vapour pressure than the expected value	5. Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.
Example: 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	Example: Acetone + aniline; acetone + chloroform; $\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$; $\text{H}_2\text{O} + \text{HNO}_3$ chloroform + diethyl ether; water + HCl; acetic acid + pyridine chloroform + benzene

Graphical representation of ideal and non-ideal solutions

