Chapter 6

Solutions

SOLUTIONS

A homogeneous mixture of two or more non-reacting substances is known as solution. Homogeneity or heterogeneity depends upon particle size and states of matter present in the solution. Every solution is made up of a solvent (present in larger quantity) and one or more solute (present in smaller quantity).

UNITS OF CONCENTRATION

(i) Molarity (M)

It is the number of moles of solute present per litre of solution.

$$M = \frac{n}{V} = \frac{w}{M_w \times V_{\text{in litre}}} = \frac{W \times 1000}{M_w \times V_{\text{in cc}}}$$

$$M \times V_{\text{in cc}} = \frac{W}{M_w} \times 1000$$

$\Rightarrow$ M × V (ml) = millimoles

Molarity changes with temperature of the solution. Increase in temperature generally decreases the molarity. It is the most convenient method to express concentration of the solution. On dilution, molarity decreases.

(ii) Molality (m) :

Number of moles (n) of solute present per kg of solvent

$$m = \frac{n}{W_{\text{in kg}}} = \frac{w}{M \times W_{\text{in kg}}} = \frac{w}{M \times W_{\text{in g}}(\text{solvent})} \times 1000$$

It is independent of temperature since no volume factor is involved in the equation.

(iii) Mole fraction (x)

It is the ratio of number of moles of one component to the total number of moles present in the solution.

For a system having two components A and B,

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

$$\therefore \boxed{X_A + X_B = 1}$$

Mole fraction is also independent of temperature.

(iv) In terms of %

$$\% \text{ by weight} = \frac{\text{Wt. of solute}}{\text{Wt. of solution}} \times 100$$

$$\% \text{ weight by volume} = \frac{\text{Wt. of solute}}{\text{Vol. of solution}} \times 100 \text{ (In case of solid dissolved in a liquid)}$$

$$\% \text{ by volume} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100 \text{ (In case of liquid dissolved in another liquid)}$$

$$\text{PPM} = \frac{\text{No. of parts of solute}}{\text{No. of parts of solution}} \times 10^6$$

% by weight is independent of temperature while % by volume are temperature dependent.

HENRY'S LAW

Solubility of a gas at a given temperature in a solvent is directly proportional to its partial pressure. If P is the partial pressure of a gas and X_g is its mole fraction in solution. Then $P = K_H X_g$ where K_H is Henry's law constant for that gas

VAPOUR PRESSURE AND RAOULT'S LAW

The pressure exerted by the vapours at the free surface of liquid (provided system is closed) is known as its vapour pressure. The V.P. of a pure liquid is always greater than its solution (In case of non-volatile solute).

(a) Raoult's Law for a solution having non-volatile solute

$$X_{\text{solute}} = \frac{P^o - P_s}{P^o}$$

$$\begin{bmatrix} x_{\text{solute}} \rightarrow \text{Mole fraction of solute in solution} \\ P^o \rightarrow \text{V.P. of pure solvent} \\ P_s \rightarrow \text{V.P. of solution} \end{bmatrix}$$

i.e., relative lowering of vapour pressure is equal to the mole fraction of solute.

(b) **Raoult's Law of miscible liquid-liquid solution**

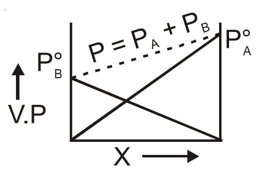
For ideal solution the partial vapour pressure is directly proportional to their mole fraction at constant temperature. For two components *A* and *B* in liquid solution.

$$P_A \propto X_A$$

$$\Rightarrow P_A = P_A^{\circ} X_A$$

$$P_B \propto X_B$$

$$\Rightarrow P_B = P_B^{\circ} X_B$$

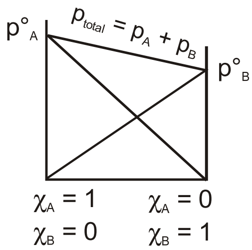
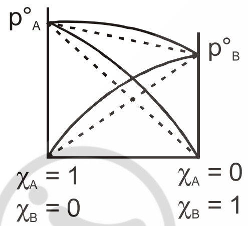
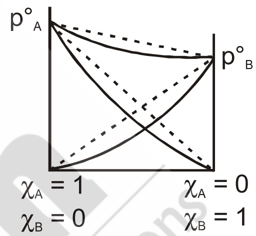


The total pressure $P = P_A + P_B = P^{\circ}_A X_A + P^{\circ}_B X_B$.

Most of the solutions show appreciable deviations from ideal behaviour known as real or non ideal solution. In some cases the deviation is +ve while in some cases deviation is –ve.

IDEAL AND NON-IDEAL SOLUTIONS

The solutions which obey Raoult's law are ideal solutions and those which do not obey Raoult's law form non-ideal solution.

Ideal Solution	Non-Ideal Solution	
	Positive Deviation	**Negative Deviation**
1. Obey's Raoult's law	1. Disobey Raoult's law	1. Disobey Raoult's law
2. $p_A = p^\circ_A.\chi_A$ $p_B = p^\circ_B\,\chi_B$ $p_{total} = p_A + p_B$	2. $p_A \neq p^\circ_A.\chi_A$ $p_B \neq p^\circ_B.\chi_B$ $p_{total} \neq p_A + p_B$ $[P_{total} > P_A + P_B]$	2. $p_A \neq p^\circ_A.\chi_A$ $p_B \neq p^\circ_B.\chi_B$ $p_{total} \neq p_A + p_B$ $[P_{total} < P_A + P_B]$
3. $\Delta H_{mix} = 0$ $\Delta G_{mix} = -ve$ $\Delta V_{mix} = 0$ $\Delta S_{mix} = +ve$	3. $\Delta H_{mix} = +ve$ $\Delta G_{mix} = -ve$ $\Delta V_{mix} = +ve$ $\Delta S_{mix} = +ve$	3. $\Delta H_{mix} = -ve$ $\Delta G_{mix} = -ve$ $\Delta V_{mix} = -ve$ $\Delta S_{mix} = +ve$
4. Interaction A – B = A – A = B – B *e.g.*, Chlorobenzene + Bromobenzene	4. Interaction A – B < A – A and B – B *e.g.*, $CH_3OH + H_2O$	4. Interaction A – B > A – A and B – B *e.g.*, $CH_3COCH_3 + CHCl_3$
		

COLLIGATIVE PROPERTIES

A colligative property of a solution is one that depends on the number of particles of solute in solution.

(a) Relative lowering of vapour pressure, $\frac{p^\circ - p_s}{p^\circ} = \chi_{solute}$.

(b) Osmotic pressure, π = CRT.

(c) Elevation of boiling point, $\Delta T_b = k_b m$.

(d) Depression in freezing point, $\Delta T_f = k_f m$.

(a) Relative lowering of V.P. : The relative lowering in V.P. of an ideal solution is equal to the mole fraction of solute at that temperature.

$$\frac{p^o_A - p_A}{p^o_A} = \chi_B = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} = \left(\frac{w_2}{M_2} \times \frac{M_1}{w_1}\right) \text{ for dilute solutions.}$$

Determination of molecular masses by relative lowering in vapour pressure.

$$\frac{p^o - p_A}{p^o_A} \simeq \frac{w}{m} \times \frac{M}{W}$$

w = Wt. of solute

m = Mol. wt. of solute

W = Wt. of solvent

M = Mol. wt. of solvent

(b) Osmotic pressure : The excess pressure which must be applied on a solution to prevent the passage of solvent into it through a semipermeable membrane.

Determination is done using Barkley-Hartley method:

Semipermeable membrane → egg membrane;

Chemical Semipermeable membrane → cupric ferrocyanide.

π = CRT = n/V. RT; πV = nRT : Van't Hoff equation for dilution solutions

$$n = \frac{w_2}{M_2}; \; M_2 = \frac{w_2.RT}{\pi V}$$

For isotonic solutions $\pi_1 = \pi_2$

Molal elevation constant or ebullioscopic constant, K_b. It is the increase in boiling point when the molality of the solution is unity.

$\Delta T_b = K_b m$, when, m = 1, $\Delta T_b = K_b$

$$M_B = \frac{W_B \times 1000}{\Delta T_b \times W_A} \times K_b$$

$$K_b = \frac{MRT_b^2}{1000 \times \Delta H_{vap}}$$

Molal depression constant. or **cryoscopic constant (K_f)**. It is the decrease in freezing point when the molality of solution is unity

$\Delta T_f = K_f.m$

when, m = 1, $\Delta T_f = K_f$

$$M_B = \frac{W_B}{\Delta T_f \times W_A} \times 1000 \times K_f$$

$$K_f = \frac{MRT_f^2}{1000 \times \Delta H_{fusion}}$$

K_b and K_f are intensive properties of solvent and do not depend upon the quantity and nature of solute.

ABNORMAL MOLECULAR MASS AND Van't HOFF FACTOR (*i*)

$$i = \frac{\text{Experimental values of Colligative property}}{\text{Calculated value of colligative property}}$$

$$= \frac{\text{Observed value of Colligative property}}{\text{Normal value of the same property}}$$

$$= \frac{\text{Normal moleculer mass}}{\text{Observed moleculer mass}}$$

$$= \frac{M_{cal}}{M_{obs}}$$

Since,

$$\text{Colligative property} \propto \frac{1}{\text{Molecular mass of solute}}$$

if i = 1, no molecular association or dissociation takes place

if i < 1, molecular association takes place

if i > 1, molecular dissociation takes place.

For substances undergoing association or dissociation in the solution.

$$\boxed{\Delta T_b = iK_b \times m}$$

$$\boxed{\Delta T_f = iK_f \times m}$$

$$\boxed{\pi = iCRT}$$

Relation between degree of association or dissociation (α) & Van't Hoff's factor (*i*)

For association $i = 1 + \alpha\left(\frac{1}{n} - 1\right)$ or $\alpha = \frac{n(i-1)}{1-n}$

where *n* = Number of particles that associate.

For dissociation $i = 1 + \alpha(n - 1)$ or $\alpha = \frac{i-1}{n-1}$

where *n* = Number of particles obtained on dissociation.

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