

Solutions

C1A Solution : Solution is a mixture of two or more non-reacting pure substances in which composition may be altered within certain limits.

There are two types of solution. They are :

- (a) Homogeneous solution (b) Heterogeneous solution

HOMOGENEOUS SOLUTIONS : In homogeneous solutions, the components are completely miscible with each other i.e, they are single phase solution. In this case, the components of the solution will lose their individuality and, therefore, they cannot be separated by filtration, setting or centrifugal action.

HETEROGENEOUS SOLUTION : In heterogeneous solutions, the components are not miscible i.e., they are multiple phase solutions. The components of these mixture can be easily separated through filtration, settling or centrifugal action.

C1B Types of solution : Depending upon the physical state of solvent and solute, there are nine type of solutions. They

Number	Solute (S ₂)	Solvent (S ₁)	Examples
1	Gas	Gas	(H ₂ + N ₂ + O ₂ : Air)
2	Liquid	Gas	Water vapours in air, Mist
3	Solid	Gas	Smoke
4	Gas	Liquid	HCl in water, CO ₂ in water
5	Liquid	Liquid	C ₂ H ₅ OH in water, n-hexane in benzene
6	Solid	Liquid	Sugar in water, urea in water
7	Gas	Solid	Pd/H ₂ ; Pt/O ₂ ; Pt/Cl ₂ ; Ni/H ₂
8	Liquid	Solid	Hg in Zn, Hg in Au
9	Solid	Solid	Alloys

Out of these nine solutions, there are the most important. They are :

- (i) Gas in Liquids (ii) Liquid in Liquid, and (iii) Solid in liquid

C1C Methods of Expressing Concentration of a Solution

Name	Symbol	Definition	Formula
Volume Percent	C	amount of solute present in 100 mL of sol.	$C = \frac{100w_1}{V}$
Weight %	%	amount of solute present in 100 g of sol.	$\% = \frac{100w_1}{w_1 + w_2}$
Molarity	M	number of mol of solution present in one L (1 dm ³ , 1000 cm ³) of solution	$M = \frac{n1000}{V}$
Molality	m	number of mol of solute present in one kg solvent	$m = \frac{n1000}{W_{\text{solvent}}}$

- * **Relation between Molarity and Molality :** $m = \frac{M \times 1000}{d - MM'}$, [d is density of solution in g/L and M' is molar mass of solute].

C2A Vapour Pressures : The pressure exerted by the vapours of a liquid which are in equilibrium with it at a

given temperature. $\log \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{2.033R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

C2B Vapour pressure of solution containing volatile or non-volatile solute : The vapour pressure of a solution depends upon the nature of the solute i.e., whether it is volatile or not.

Case I : When the solute is non-volatile (Lowering in vapour pressure)

Raoult's Law : It is stated as, "if the solute is non-volatile, then the vapour pressure of the solution is directly proportional to the mole fraction of the solvent", at a given temperature.

Assume n_A and n_B are the number of solvent and solute in a given solution.

For non-volatile solutes : $P_A = P_A^0 X_A$

P_A is the partial pressure of solvent and P_A^0 is the vapour pressure of pure solvent having mole fraction X_A

As the solute is non-volatile thus total pressure of solution and partial pressure of solvent are same.

$P = P_A^0 X_A$ P is the total pressure of solution, $\frac{P^0 - P}{P^0} = \frac{n_B}{n_A + n_B}$, $\frac{P^0 - P}{P} \times \frac{1000}{M_{\text{solvent}}} = m$

Case II : When the solution is volatile

Raoult's Law : It is stated as, "At a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component is directly proportional to their mole fraction".

For Volatile solutions : $P_A = P_A^0 X_A$ and $P_B = P_B^0 X_B$

(Total vapour pressure of solution) $P = P_A + P_B$, $P = (P_A^0 - P_B^0) X_A + P_B^0$

Mole fraction of components A and B in vapour phase is determined as $\frac{P_A^0 X_A}{P_B^0 X_B} = \frac{Y_A}{Y_B}$

- * **Ideal solution :** Which obey Raoult's law at all concentrations and follow the condition. $\Delta H_{\text{mix}} = 0$, $\Delta V_{\text{mix}} = 0$ (for liquid - liquid solution too), $\Delta S_{\text{mix}} > 0$.

- * **Non-ideal solution :** Which show positive or negative deviations from Raoult's law.

$\Delta H_{\text{mix}} = +ve$; $\Delta V_{\text{mix}} = +ve$; b.Pt is smaller than expected

Examples of solutions with positive deviations :

- (i) $C_2H_5OH + C_6H_{12}$ (ii) $CH_3COCH_3 + CS_2$ (iii) $CCl_4 + CHCl_3$
 (iv) Acetone (CH_3COCH_3) + C_2H_5OH (v) $C_2H_5OH + H_2O$

- * **Non-ideal solution with negative deviation from Raoult's Law**

$\Delta H_{\text{mix}} = -ve$; $\Delta V_{\text{mix}} = -ve$; b.Pt is higher than expected.

Examples of solutions with negative deviations :

- (i) Acetone and chloroform (ii) Chloroform and ether
 (iii) Chloroform and nitric acid (iv) Acetone and aniline
 (v) Water and nitric acid

- * **Azeotrope** : A mixture of liquids boils at a constant temperature like pure liquid and has same composition of component in liquid as well as vapours.

Practice Problems :

- Two liquids A and B have vapour pressure in the ratio $P_A^0 : P_B^0 = 2 : 3$ at a certain temperature. Assume A and B form an ideal solution and the ratio of mole fraction of A to B in the vapour phase is 1 : 3, then the mole fraction of A in the solution at the same temperature is
 (a) $\frac{1}{3}$ (b) $\frac{2}{3}$ (c) $\frac{1}{4}$ (d) $\frac{3}{4}$
- The vapour pressure of solution of 5 g of a non-electrolyte in 100 g of water at a particular temperature is 2985 Nm^{-2} . The vapour pressure of pure water at that temperature is 3000 Nm^{-2} . The molecular mass (g mol^{-1}) of the solute is
 (a) 180 (b) 90 (c) 270 (d) 200
- The vapour pressure of a pure liquid A is 40 mm Hg at 310 K. The vapour pressure of this liquid in a solution with liquid B is 32 mm Hg. Mol fraction of A in the solution, if it obeys Raoult's law, is :
 (a) 0.8 (b) 0.5 (c) 0.2 (d) 0.4
- The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be the mole fraction of solvent if decreases in vapour pressure is 20 mm of Hg
 (a) 0.8 (b) 0.6 (c) 0.4 (d) 0.2

[Answers : (1) a (2) a (3) a (4) b]

C3A Colligative properties : Properties, whose values depends only on the concentration of solute particles in solution and not on the identity of the solute are called Colligative Properties.

C3B Van't Hoff Factor 'i' : There may be change in number of mol of solute due to ionisation or association hence these properties are also affected. Number of mol of the product is related to degree of ionisation or association by van't Hoff Factor 'i' is given by

* **In case of dissociation** : $i = [1 + (n - 1)\alpha]$

where n is the number of products (ions or molecules) obtained per mol of the reactant.

* **In case of association** : $i = [1 + (\frac{1}{n} - 1)\alpha]$

where 'n' is the no. of moles of solute undergoes association and α is degree of association

$$i = \frac{\text{Theoretical molar mass}}{\text{Experimental molar mass}}$$

$$i = \frac{\text{Observed value of colligative property due to diss. or asso.}}{\text{Theoretical value of colligative property without diss. or asso.}}$$

$$i = \frac{\text{no. of moles of solute at time 't'}}{\text{initial no. of moles of solute added}}$$

if $i = 1$ (no change), $i > 1$ (dissociation), $i < 1$ (association)

Practice Problems :

- Which one of the following salt would have the same value of the Van't Hoff factor (i) as that of $K_3[Fe(CN)_6]$
 (a) NaCl (b) Na_2SO_4 (c) $Al_2(SO_4)_3$ (d) $Al(NO_3)_3$
- The van't Hoff factor of a 0.005 M aqueous solution of KCl is 1.96. The degree of dissociation of KCl at the given concentration is
 (a) 92% (b) 94% (c) 96% (d) 98%

[Answers : (1) d (2) c]

C3C There are four Colligative properties :

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

* Colligative properties are defined for only non-volatile solute.

(i) Relative lowering in vapour pressure

$$\frac{\Delta p}{p^0} = X_{\text{solute}} \dots\dots\dots [X_{\text{solute}} \text{ is mole fraction of solute}]$$

 $\Delta p = (p^0 - p)$ is lowering in vapour pressure]

$$\frac{\Delta p}{p^0} = \frac{i n_B}{i n_B + n_A} \dots\dots [n_B \text{ and } n_A \text{ are no. of moles of solutes and solvent respectively}]$$

(ii) Elevation in boiling point

$$\Delta T_b = T_b - T_b^0 = i K_b \cdot m \dots\dots [K_b \text{ is called as molal elevation constant, } m \text{ is the molality of solution}]$$

In elevation of b.Pt : b.Pt of solution (T_b) > (T_b^0) b.Pt of solvent

$$K_b = \frac{R(T_b^0)^2 M_{\text{solvent}}}{1000 \Delta H_{\text{vap}}} \dots\dots [M_{\text{solvent}} \text{ is molar mass of solvent and } \Delta H_v \text{ is the enthalpy of vaporisation per mole of solvent}]$$

(iii) Depression in freezing point :

$$\Delta T_f = T_f^0 - T_f = i K_f \cdot m \dots\dots [K_f \text{ is molal depression constant}]$$

F.Pt of solution (T_f) < (T_f^0) F.Pt of solvent

$$K_f = \frac{R(T_f^0)^2 M_{\text{solvent}}}{1000 \times \Delta H_{\text{fus}}} \dots\dots [\Delta H_f \text{ is the enthalpy of fusion per mole of solvent}]$$

(iv) Osmotic pressure (π)

Spontaneous flow of solvent from dilute solution (it may be pure solvent) into the concentrated solution through a semi permeable membrane is called osmosis.

Pressure required to prevent osmosis is called as osmotic pressure.

Copper (II) ferrocyanide, $Cu_2[Fe(CN)_6]$, warm mixture of gelatine and glycerine are common semi-permeable membranes.

$$\pi = iCRT \dots\dots [C \text{ is the molarity of the solution at temperature 'T'}]$$

* For isotonic solution $\pi_1 = \pi_2$

* For a solution $\pi_1 > \pi_2$ (hypotonic)

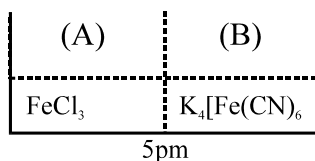
* $\pi_1 < \pi_2$ (hypertonic)

Reverse osmosis : Flow of solvent of high concentrate solution into low by the application of pressure, greater than osmotic pressure. (For desalination of sea water).

Practice Problems :

- The vapour pressure of water at room temperature is lowered by 5% by dissolving a solute in it, then the approximate molality of solution is
(a) 2 (b) 1 (c) 4 (d) 3
- A solution of glucose ($C_6H_{12}O_6$) is isotonic with 4 g of urea ($NH_2 - CO - NH_2$) per litre of solution. The concentration of glucose is
(a) 4 g/l (b) 8 g/l (c) 12 g/l (d) 14 g/l
- 1.0 molal aqueous solution of an electrolyte X_3Y_2 is 25% ionized. The boiling point of the solution is (K_b for $H_2O = 0.52 \text{ K kg/mol}$)
(a) 375.5 K (b) 374.04 K (c) 377.12 K (d) 373.25 K
- Molal depression of freezing point of water is 1.86° per 1000 g of water. 0.02 mole of urea dissolved in 100 g of water will produce a lowering of temperature of
(a) 0.186° (b) 0.372° (c) 1.86° (d) 3.72°
- Arrange the following aqueous solutions in the order of their increasing boiling points
(i) 10^{-4} M NaCl (ii) 10^{-3} M Urea (iii) 10^{-3} M MgCl_2 (iv) 10^{-2} M NaCl
(a) (i) < (ii) < (iv) < (iii) (b) (ii) < (i) = (iii) < (iv)
(c) (i) < (ii) < (iii) < (iv) (d) (iv) < (iii) < (i) = (ii)
- 1 mol each of following solutes are taken in 5 mol water,
(A) NaCl (B) K_2SO_4 (C) Na_3PO_4 (D) glucose
Assuming 100% ionisation of the electrolyte relative decrease in vapour pressure will be in the order :
(a) $A < B < C < D$ (b) $D < C < B < A$ (c) $D < A < B < C$ (d) equal
- $PtCl_4 \cdot 6H_2O$ can exist as a hydrated complex; 1 molal aq. solution has depression in freezing point of 3.72° . Assume 100% ionisation and $K_f(H_2O) = 1.86^\circ \text{ mol}^{-1} \text{ kg}$, then complex is :
(a) $[Pt(H_2O)_6]Cl_4$ (b) $[Pt(H_2O)_4Cl_2]Cl_2 \cdot 2H_2O$
(c) $[Pt(H_2O)_3Cl_3]Cl \cdot 3H_2O$ (d) $[Pt(H_2O)_2Cl_4] \cdot 4H_2O$
- The osmotic pressure of a 5% (wt./vol.) solution of cane sugar at 150°C is
(a) 4 atm (b) 3.4 atm (c) 5.078 atm (d) 2.45 atm
- Following solutions at the same temperature will be isotonic
(a) 3.42 g of cane sugar in one litre water and 0.18 g of glucose in one litre water
(b) 3.42 g of cane sugar in one litre water and 0.18 g of glucose in 0.1 one litre water
(c) 3.42 g of cane sugar in one litre water and 0.585 g of NaCl in one litre water
(d) 3.42 g of cane sugar in one litre water and 1.17 g of NaCl in one litre water
- Relative decrease in V.P. of an aqueous glucose dilute solution is found to be 0.018. Hence elevation in boiling point is : (it is given 1 molal aq. urea solution boils at 100.54°C at 1 atm. pressure).
(a) 0.018 $^\circ$ (b) 0.18 $^\circ$ (c) 0.54 $^\circ$ (d) 0.03 $^\circ$

11. Two solutions (A) containing $\text{FeCl}_3(\text{aq})$ and (B) containing $\text{K}_4\text{Fe}(\text{CN})_6$ are separated by semipermeable membrane as shown below. If FeCl_3 on reaction with $\text{K}_4\text{Fe}(\text{CN})_6$ produces blue



colour of $\text{Fe}_4\text{Fe}(\text{CN})_6$, the blue colour will be noticed in

- (a) (A) (b) (B)
 (c) In both (A) and (B) (d) Neither in (A) nor in (B)
12. 10 g. of solute A and 20 g. of solute B are both dissolved in 500 ml. of water. The solution has the same osmotic pressure as 6.67 g of A and 30 g of B are dissolved in the same volume of water at the same temperature. Thus the ratio of molar masses of A and B is
 (a) 3.33 (b) 3 (c) 10 (d) 0.33
13. At 25°C , the osmotic pressure of human blood due to the pressure of various solutes in the blood is 7.65 atm. Assuming that molarity and molality are almost same. The freezing point of blood is [$K_f = 1.86 \text{ K kg/mol}$].
 (a) 0.582°C (b) -0.582°C (c) 1.582°C (d) -1.582°C

[Answers : (1) d (2) c (3) b (4) b (5) c (6) c (7) c (8) c (9) b (10) c (11) d (12) b]