
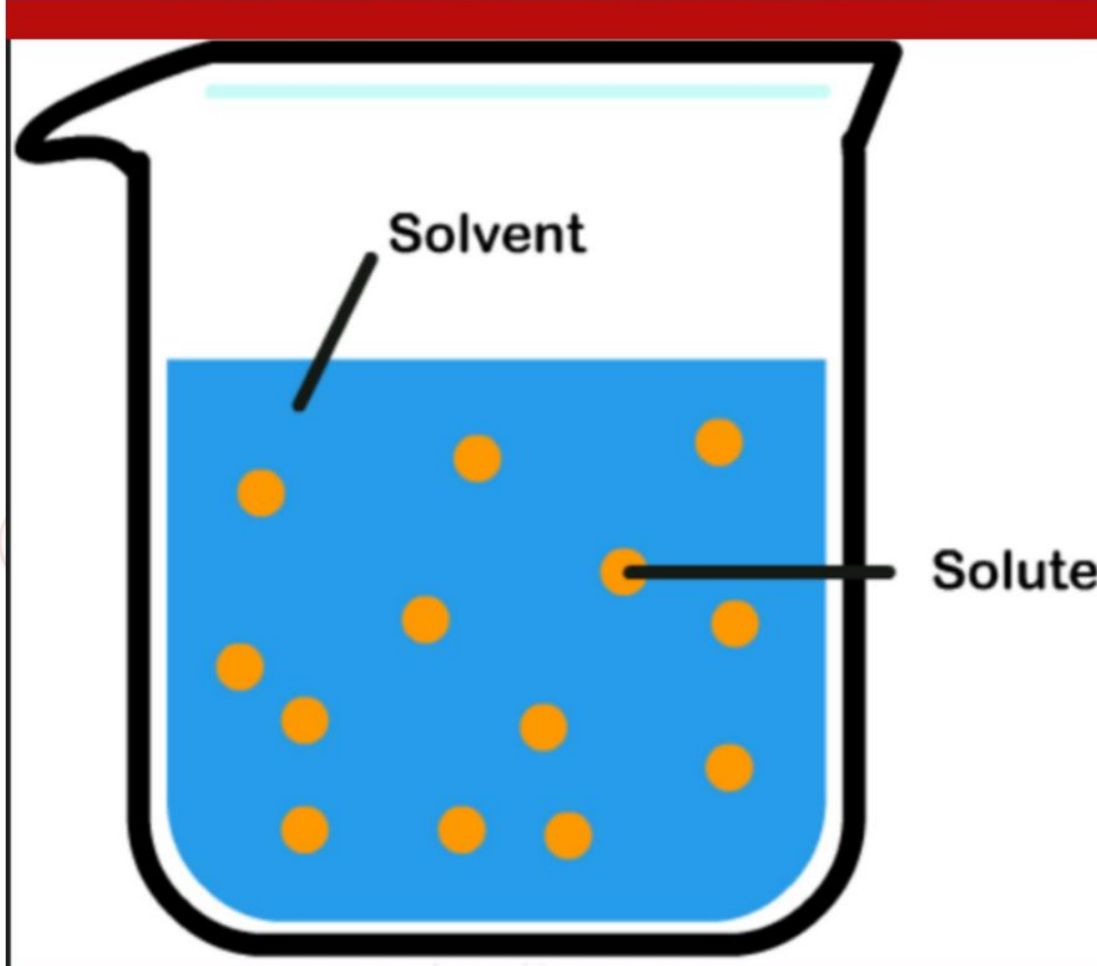


## UNIT I: SOLUTIONS



A row of laboratory glassware including beakers, flasks, and test tubes containing liquids of various colors: blue, purple, orange, green, yellow, red, and green.

# SOLUTIONS



A diagram of a beaker containing a blue liquid. Several orange dots are scattered throughout the liquid. A label 'Solvent' points to the blue liquid, and a label 'Solute' points to one of the orange dots.

**Solute + Solvent = SOLUTION**



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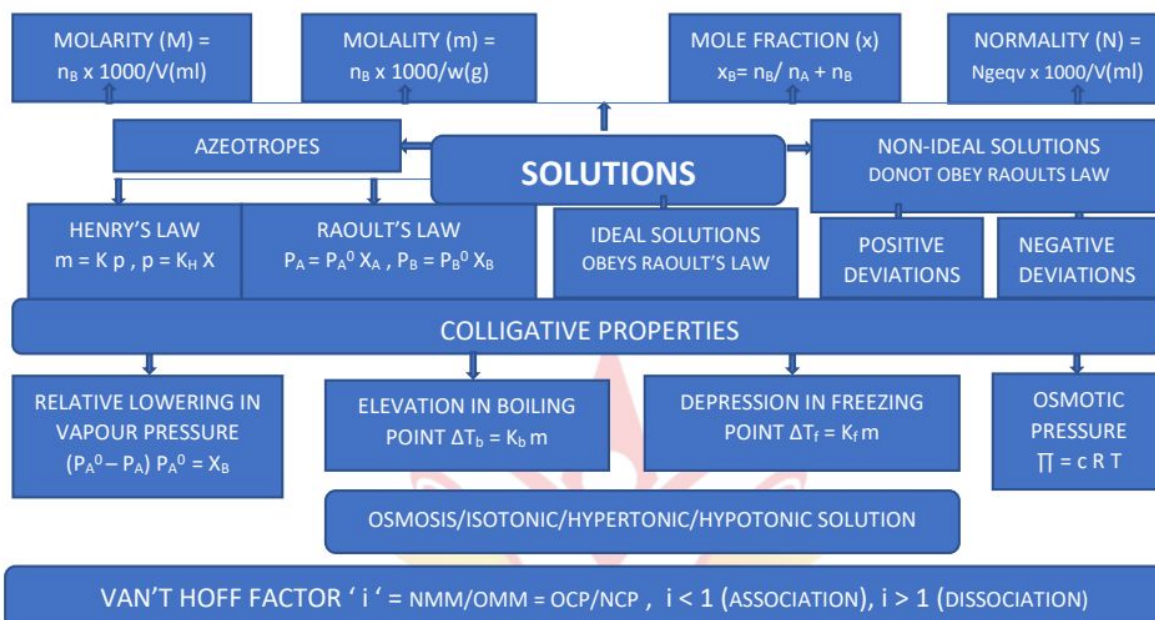
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A **solution** is a homogeneous mixture of two or more chemically non-reacting substances. Solutions are the homogeneous mixtures of two or more than two components. A solution having two components is called a **binary solution**. It includes **solute and solvent**.

A solution may be classified as **solid, liquid or a gaseous solution**.

#### Types of Solutions:

Type of solution	Solute	Solvent	Common examples
<b>Solid solutions</b>	Solid	Solid	Copper dissolved in gold
	Liquid	Solid	Amalgam of mercury with sodium
	Gas	Solid	Solution of hydrogen in palladium
<b>Liquid Solutions</b>	Solid	Liquid	Glucose dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Gas	Liquid	Oxygen dissolved in water
<b>Gaseous Solution</b>	Solid	Gas	Camphor in nitrogen gas
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Gas	Gas	Mixture of oxygen and nitrogen gases

**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.

$$\text{Mass \% of component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$$

**Molality (m):** It is the number of moles of solute present in 1kg of solvent.

$$\text{Molality (m)} = \frac{\text{Mass of solute (w)}}{\text{Molar mass of solute} \times \text{Mass of solvent (g)}} \times 1000$$

**Molarity (M):** It is the number of moles of solute present in 1L of solution.

$$\text{Molarity (M)} = \frac{\text{Mass of solute (w)}}{\text{Molar mass of solute} \times \text{Volume of solution (ml)}} \times 1000$$

**Normality:** It is the number of gram equivalent of solute dissolved per litre of solution.

$$\text{Normality (N)} = \frac{\text{No. of gm. equiv. of solute}}{\text{Volume of solution (ml)}} \times 1000$$

**Saturated solution:** It is a solution in which no more solute can be dissolved at the same temperature and pressure. If dissolution process is an endothermic process, solubility increases with increase in temperature. If dissolution process is an exothermic process, solubility decreases with increase in temperature.

**Solubility** is defined as the amount of solute in a saturated solution per 100g of a solvent. The **solubility of a gas in a liquid** depends upon:

- (a) the nature of the gas and the nature of the liquid,
- (b) the temperature of the system, and
- (c) the pressure of the gas.

The **effect of pressure on the solubility of a gas in a liquid** is governed by **Henry's Law**: It states that the solubility of a gas in a liquid at a given temperature is directly proportional to the partial pressure of the gas

$$p = K_H \times x$$

Where  $p$  is the partial pressure of the gas; and  $x$  is the mole fraction of the gas in the solution and  $K_H$  is Henry's Law constant.

The **vapour pressure of a liquid** is the pressure exerted by its vapour when it is in dynamic equilibrium with its liquid, in a closed container.

**Raoult's Law**, the vapour pressure of a solution containing a non-volatile solute is directly proportional to the mole fraction of the solvent ( $X_A$ ). The proportionality constant being the vapour pressure of the pure solvent,

$$P_A \propto X_A$$

$$P_A = P_A^\circ X_A$$



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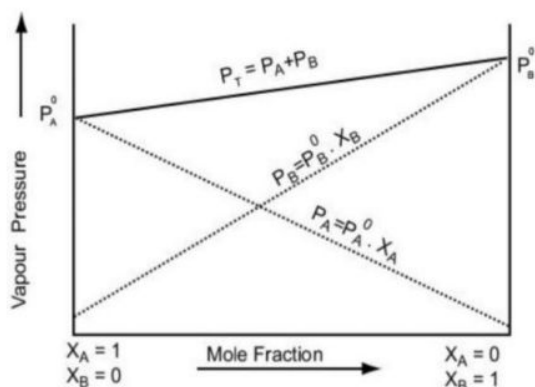


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$$P_A = P_A^0 X_A$$

$$P_B = P_B^0 X_B$$

$$\begin{aligned} P_A + P_B &= P_A^0 X_A + P_B^0 X_B \\ &= P_A^0 (1 - X_B) + P_B^0 X_B \quad [X_A + X_B = 1] \\ &= P_A^0 - P_A^0 X_B + P_B^0 X_B \\ P_{\text{total}} &= P_A^0 + (P_B^0 - P_A^0) X_B \end{aligned}$$

The binary liquid in liquid solutions can be classified into two types; ideal and non-ideal solutions.

**Ideal Solution:** An ideal solution is a solution where the intermolecular interactions between solute-solute (A-A) and solvent-solvent (B-B) are similar to the interaction between solute-solvent (A-B). An ideal solution fulfils the following criteria:

- It obeys Raoult's law for all the concentration and temperature ranges. This states that the partial vapour pressure of each component is proportional to the mole fraction of the component in a solution at a given temperature.
- The enthalpy of mixing is zero, i.e.,  $\Delta H_{\text{mix}} = 0$ . It means that no heat is absorbed or released.
- The volume of mixing is zero,  $\Delta V_{\text{mix}} = 0$ . It means that the volume of the solution is equal to the sum of the volume of components.

The ideal solution is possible with components of the same size and polarity. There is no association, dissociation or reaction taking place between components. A perfect ideal solution is rare but some solutions are near to the ideal solution. Examples are Benzene and toluene, hexane and heptane, Bromoethane and Chloroethane, Chlorobenzene and bromobenzene, etc.

#### Non-ideal Solution:

- When a solution does not obey Raoult's law for all the concentration and temperature ranges it is known as a non-ideal solution. A non-ideal solution may show positive or negative deviation from Raoult's law.
- $\Delta H_{\text{mix}} \neq 0$
- $\Delta V_{\text{mix}} \neq 0$

#### (a) Non-ideal solution showing positive deviation

Here the total vapour pressure is higher than that calculated from Raoult's equation. The interaction between solute-solvent (A-B) is weaker than those of pure components (A-A or B-B). The  $\Delta H_{\text{mix}}$  and  $\Delta V_{\text{mix}}$  are positive. E.g., ethanol and acetone, carbon disulphide and acetone, acetone and benzene, etc



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**(b) Non-ideal solution showing negative deviation**

Here the total vapour pressure is lower than that calculated from Raoult's equation. The interaction between solute-solvent (A-B) is stronger than those of pure components (A-A or B-B). The  $\Delta H_{\text{mix}}$  and  $\Delta V_{\text{mix}}$  are negative. E.g., phenol and aniline, chloroform and acetone, etc.

**Difference between Ideal and Non-ideal Solution**

S.No.	Ideal Solution	Non-ideal Solution
1	They obey Raoult's law	They do not obey Raoult's law
2	Intermolecular interaction between solute and solvent is the same as that of pure components	Intermolecular interaction between solute and solvent is weaker or stronger than that of between pure components
3	The total vapour pressure is the same as predicted from Raoult's law	The total vapour pressure increases or decreases from the predicted value according to Raoult's law
4	No heat is released or absorbed so the enthalpy of mixing is zero, $\Delta H_{\text{mix}} = 0$	Heat is either absorbed or released so the enthalpy of mixing is either positive or negative, $\Delta H_{\text{mix}} \neq 0$
5	The total volume is equal to the sum of the volume of components (solute and solvent) so the volume of mixing is zero, $\Delta V_{\text{mix}} = 0$	The volume of mixing is not zero, $\Delta V_{\text{mix}} \neq 0$ . There is either expansion or contraction.
6	Components can be separated by fractional distillation	Components can't be separated in the pure form by fractional distillation
7	Does not form an azeotrope	Forms azeotrope mixture
8	Examples: Benzene and toluene, hexane and heptane, etc. All the dilute solutions nearly behave as an ideal solution	Examples: Ethanol and acetone, carbon disulphide and acetone, phenol and aniline, chloroform and acetone, etc.

**Colligative properties of solutions** are those properties which depend only upon the number of solute particles in the solution and not on their nature.

Such properties are:

- (a) Relative lowering in vapour pressure,
- (b) Elevation of boiling point,
- (c) Depression of freezing point and
- (d) Osmotic pressure.

**(a) Relative lowering in vapour pressure:** According to Raoult's Law, the relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute.

$$(P_A^0 - P_A)/P_A^0 = X_B = n_B / (n_A + n_B)$$

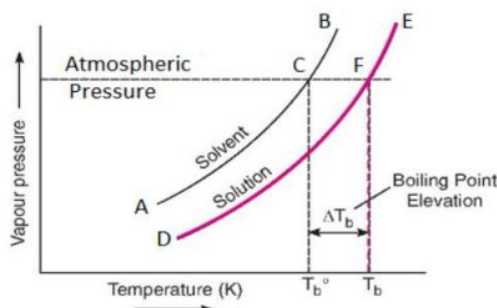
$$(P_A^0 - P_A)/P_A^0 = (w_B/M_B)/W_A/M$$

$$M_B = \frac{w_B M_A}{w_A (P_A^0 - P_A)/P_A^0}$$

**(b) Elevation of boiling point:** Boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. The boiling point of the pure solvent is  $T_b^0$  while that of the

solution is  $T_b$ . Since,  $T_b$  is greater than  $T_b^0$ , there is an elevation or increase in boiling temperature of the solution as compared to that of solvent. The elevation in boiling point,  $\Delta T_b$  may be expressed as:

$$\Delta T_b = T_b - T_b^0$$



The **elevation in boiling point** is found to be proportional to the molality of the solution.

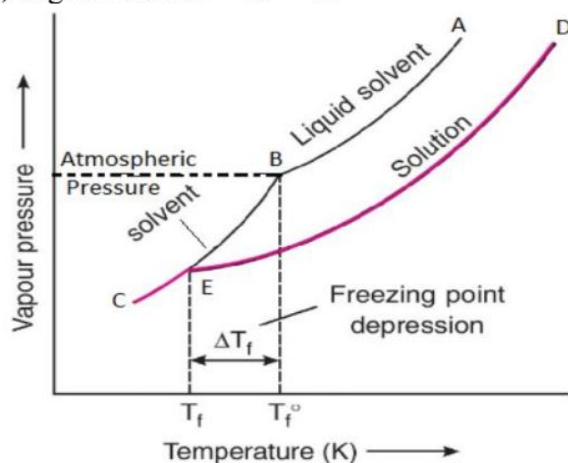
$$\Delta T_b \propto m$$

$\Delta T_b = K_b m$ , where  $\Delta T_b$  is the elevation in boiling point, 'm' is the molality and  $K_b$  is the Molal elevation constant

$$\Delta T_b = K_b m = (K_b \times w_B \times 1000) / M_B \times w_A$$

$$M_B = \frac{(K_b \times w_B \times 1000)}{\Delta T_b \times w_A}$$

**(c) Depression of freezing point:** Freezing point is the temperature at which the solid and the liquid states of the substance have the same vapour pressure. Freezing point temperature of pure solvent is  $T_f^0$  and freezing point temperature of the solution is  $T_f$ . The  $T_f$  is less than  $T_f^0$ . This shows that the freezing temperature of the solution is less than that of pure solvent and the depression in freezing temperature ( $\Delta T_f$ ) is given as:  $\Delta T_f = T_f^0 - T_f$



The **depression in freezing point** ( $\Delta T_f$ ) is proportional to the molality of the solution.

$$\Delta T_f \propto m$$

$\Delta T_f = K_f m$  Where  $K_f$  is molal depression constant (freezing point depression constant).

$$\Delta T_f = K_f m = (K_f \times w_B \times 1000) / M_B \times w_A$$



$$M_B = \frac{(K_f \times w_B \times 1000)}{\Delta T_f \times w_A}$$

**Osmosis:** The spontaneous flow of solvent molecules from a dilute solution into a concentrated solution when the two are separated by a perfect semipermeable membrane.

**(d) Osmotic pressure ( $\pi$ )** is the pressure which must be applied to the solution side (more concentrated solution) to just prevent the passage of pure solvent into it through a semipermeable membrane. According to Van't Hoff equation,

$$\pi = cRT = (n_B/V) RT = (w_B/M_B V) RT$$

$$M_B = \frac{w_B RT}{\pi V}$$

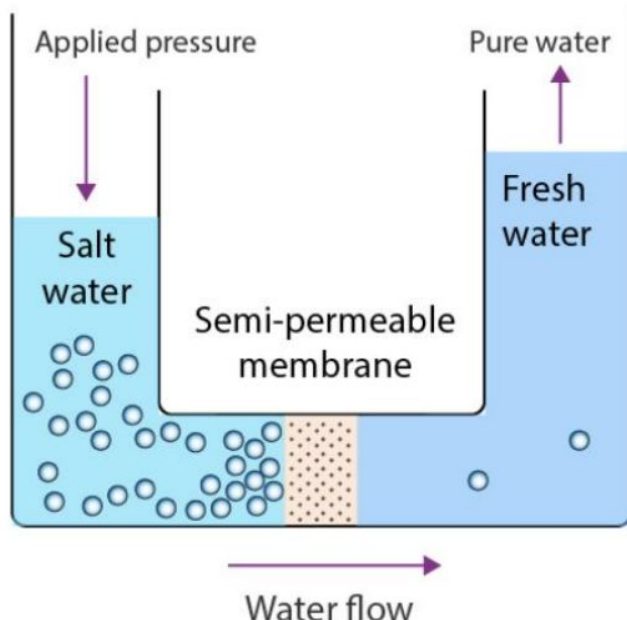
where  $n$  is the osmotic pressure of the solution,

$C$  is the concentration of solution,  $n_B$  is the number of moles of solute,  $M_B$  is the molar mass of the solute,  $V$  is the volume of the solution in liters,

$R$  is the gas constant, and  $T$  is the temperature on the Kelvin scale.

#### Reverse Osmosis:

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called reverse osmosis



**Isotonic solutions** are those solutions which have the same osmotic pressure. Also, they have same molar concentration.

For isotonic solutions,  $\pi_1 = \pi_2$  Also,  $C_1 = C_2$

**Hypertonic solutions** if a solution has more osmotic pressure than some other solutions.

**Hypotonic solutions** if a solution has less osmotic pressure than some other solutions.

**Abnormal molecular mass:** A molar mass that is either lower or higher than the expected or normal value is called as abnormal molar mass.

**Van't Hoff factor:** In 1880 Van't Hoff introduced a factor  $i$ , known as the Van't Hoff factor, to account for the extent of dissociation or association. This factor  $i$  is defined as:

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

$$= \text{Observed colligative property} / \text{Calculated colligative property}$$

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

Here abnormal molar mass is the experimentally determined molar mass and calculated colligative properties are obtained by assuming that the non-volatile solute is neither associated nor dissociated.

In case of association, value of  $i$  is less than unity while for dissociation it is greater than unity.

For example, the value of  $i$  for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.

Inclusion of Van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent,

$$(P_A^0 - P_A)/P_A^0 = iX_B$$

Elevation of Boiling point,  $\Delta T_b = i K_b m$

Depression of Freezing point,  $\Delta T_f = i K_f m$

Osmotic pressure of solution,  $\pi = i n_B R T / V$

Values of  $i$  for KCl, NaCl, MgSO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>

Salt	Van't Hoff Factor $i$ for complete dissociation of solute
KCl	2
NaCl	2
MgSO <sub>4</sub>	2
K <sub>2</sub> SO <sub>4</sub>	3

### Assignment:

1. The atmospheric pollution is generally measured in the units of

- (a) mass percentage
- (b) volume percentage
- (c) volume fraction
- (d) ppm

Ans. (d) ppm

2. Temperature dependent term among the following is –

- (a) Molality
- (b) Molarity
- (c) Mole fraction



(d) Weight percentage

Ans. (b) Molarity

3. The law which indicates the relationship between solubility of a gas in liquid and pressure is

- (a) Raoult's law
- (b) Henry's law
- (c) Lowering of vapour pressure
- (d) Van't Hoff law

Ans. (b) Henry's law

4. Partial pressure of a solution component is directly proportional to its mole fraction. This is known as

- (a) Henry's law
- (b) Raoult's law
- (c) Distribution law
- (d) Ostwald's dilution law

Ans. (b) Raoult's law

5. Which of the following solutions shows positive deviation from Raoult's law?

- (a) Acetone + Aniline
  - (b) Acetone + Ethanol
  - (c) Water + Nitric acid
  - (d) Chloroform + Benzene
- Ans. (b) Acetone + Ethanol

6. The system that forms maximum boiling azeotrope is

- (a) Acetone-chloroform
- (b) ethanol-acetone
- (c) n-hexane-n-heptane
- (d) carbon disulphide-acetone

Ans. (a) Acetone-chloroform

7. A plant cell shrinks when it is kept in a

- (a) hypotonic solution
- (b) hypertonic solution
- (c) isotonic solution
- (d) pure water

Ans. (b) hypertonic solution

8. The osmotic pressure of a solution can be increased by

- (a) increasing the volume



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- (b) increasing the number of solute molecules
- (c) decreasing the temperature
- (d) removing semipermeable membrane

Ans. (b) increasing the number of solute molecules

9. Sprinkling of salt helps in clearing the snow-covered roads in hills. The phenomenon involved in the process is

- (a) lowering in vapour pressure of snow
- (b) depression in freezing point of snow
- (c) melting of ice due to increase in temperature by putting salt
- (d) increase in freezing point of snow

Ans. (b) depression in freezing point of snow

10. The Van't Hoff factor [i] for a dilute aqueous solution of the strong electrolyte barium hydroxide is?

- (a) 0
- (b) 1
- (c) 2
- (d) 3

Ans. (d) 3

Q11. If  $1.202 \text{ g mL}^{-1}$  is the density of 20% aqueous KI, determine the following:

- (a) Molality of KI
- (b) Molarity of KI
- (c) Mole fraction of KI

Ans. 20% solution of KI means 20g of KI are present in 100g of solution or 80g of water.

- (a) Molar mass of KI = 166

$$\text{Moles of KI} = 20/166 = 0.120$$

$$\text{Molality} = 0.120 \times 1000 / 80 = 1.5 \text{ m}$$

- (b) Volume of solution =  $100/1.202 = 83.19 \text{ ml}$

$$\text{Molarity} = 0.120 \times 1000 / 83.19 = 1.44 \text{ M}$$

- (c) Moles of KI =  $20/166 = 0.120$

$$\text{Moles of water} = 80/18 = 4.44$$

$$\text{Mole fraction of KI} = 0.120/(4.44+0.120) = 0.0263$$

Q12. Calculate Henry's law constant when the solubility of  $\text{H}_2\text{S}$  (a toxic gas with rotten egg like smell) in water at STP is 0.195 m

Ans. Moles of  $\text{H}_2\text{S}$  = 0.195

$$\text{Moles of water} = 1000/18 = 55.55$$

$$\text{Mole fraction of } \text{H}_2\text{S} = 0.195 / (55.55+0.195) = 0.0035$$

$$p = K_H \times x_2$$

$$K_H = p / x_2 = 0.987 \text{ bar} / 0.0035 = 282 \text{ bar}.$$

Q13. 18g of glucose,  $C_6H_{12}O_6$ , is dissolved in 1 kg of water in a sauce pan. At what temperature will the water boil.  $K_b$  for water is  $0.52 \text{ K kg mol}^{-1}$  and boiling point of water is  $373.15 \text{ K}$ .

$$\text{Ans. } \Delta T_b = K_b m = (K_b \times w_B \times 1000) / M_B \times w_A$$

$$(0.52 \times 18 \times 1000) / (180 \times 1000) = 0.052$$

$$\text{boiling point of the solution} = 373.15 + 0.052 = 373.202 \text{ K}$$

Q14. 2 g of benzoic acid ( $C_6H_5COOH$ ) dissolved in 25 g of benzene shows a depression in freezing point equal to  $1.62 \text{ K}$ . Molal depression constant for benzene is  $4.9 \text{ K kg mol}^{-1}$ . What is the percentage association of acid if it forms dimer in solution?

$$\text{Ans. } \Delta T_f = K_f m = (K_f \times w_B \times 1000) / M_B \times w_A$$

$$M_B = (4.9 \times 2 \times 1000) / (1.62 \times 25) = 241.98 \text{ g mol}^{-1}$$

$$\text{Molar mass of } C_6H_5COOH = 122 \text{ g mol}^{-1}$$



Initial moles

1

0

Moles after association

$(1 - \alpha)$

$\alpha/2$

Total moles after association =  $1 - \alpha + \alpha/2 = 1 - \alpha/2$

$$i = \text{Normal molar mass} / \text{Observed molar mass} = 122 / 241.98 = 0.504$$

$$i = (1 - \alpha/2) / 1 = 0.504$$

$$\alpha = 0.992$$

Thus, the degree of association of benzoic acid in benzene = 99.2%

Q15. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of  $K_2SO_4$  in 2 litres of water at  $25^\circ \text{ C}$ , assuming that it is completely dissociated.

Ans. If  $K_2SO_4$  is completely dissociated, then  $i = 3$

$$\text{Molar mass of } K_2SO_4 = 174$$

$$\pi = i cRT = i (n_B/V) RT = i (w_B RT / M_B V)$$

$$= 3 \times 25 \times 10^{-3} \times 0.082 \times 298 / 174 \times 2$$

$$\pi = 5.27 \times 10^{-3} \text{ atm.}$$