
LESSON AT A GLANCE

- **Solution:** A solution is a homogenous mixture of two or more pure substances whose composition may be altered within certain limits.
- **Concentration of solution:** The concentration of a solution is expressed in terms of mole fraction, molarity, molality and in percentages.
- **Henry's law:** At a given temperature the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas.
- **Lowering of vapour pressure:** The vapour pressure of the solvent is lowered by the presence of a non-volatile solute in the solution and this lowering of vapour pressure of the solvent is governed by Raoult's law.
- **Raoult's law:** Relative lowering of vapour pressure of the solvent over a solution is equal to the mole fraction of a non-volatile solute present in the solution.
- **Ideal solution:** Solution which obeys Raoult's law over the entire range of concentration are called ideal solution. Two types of deviation from Raoult's law are called *positive deviation* and *negative deviation*.
- **Azeotropes:** Liquid mixture which distill over without changes in composition are called *constant boiling mixtures* or *Azeotropes* or *Azeotropic mixture*.
- **Colligative properties** have been used to determine the molar mass of solutes.
- **Abnormal molar mass:** Solutes which dissociate in solution exhibit molar mass lower than the actual molar mass and those which associate show higher molar mass than their actual values.

- **Van't Hoff factor:** A factor appearing in equations for colligative properties, equal to the ratio of the number of actual particles present to the number of undissociated particles, it was first suggested by Jacobus van't Hoff (1852-1911), can be expressed by Van't Hoff factor symbol i .

This factor has been defined as ratio of normal molar mass to experimentally determined molar mass or as the ratio of observed colligative property to the calculated colligative property.

- **Solutions:** Solutions are homogeneous mixtures of two or more than two components.
- **Solvent:** Component that is present in the largest quantity in a solution is known as *solvent*.
- **Solute:** One or more component present in the solution other than solvent are called *solutes*.
- **Binary Solution:** Those solutions which contain two components are called *binary solutions*, e.g. salt solution, benzene, and toluene.
- **Aqueous solution:** When solute is dissolved in water, it is called *aqueous solution*, e.g. sugar solution, ethanol in water.
- **Non-aqueous solution:** When the solute is dissolved in solvent other than water, it is called *non-aqueous solution*, e.g. iodine dissolved in alcohol. (Tincture of iodine).

TEXTBOOK QUESTIONS SOLVED

- 2.1** Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.

Ans. A solution is a homogeneous mixture of two or more substances which are chemically nonreacting. On the basis of physical component solutions are of the following types:

Solid Solution

S.No.	Solute	Solvent	Types of solution	Examples
1.	Solid	Solid	Solid in solid	All alloys like brass
2.	Liquid	Solid	Liquid in solid	Amalgum of mercury with Na
3.	Gas	Solid	Gas in solid	Solution of H_2 in Pd

Liquid Solution

S.No.	Solute	Solvent	Types of solution	Examples
1.	Solid	Liquid	Solid in liquid	Sugar solution
2.	Liquid	Liquid	Liquid in liquid	Benzene in toluene
3.	Gas	Liquid	Gas in liquid	CO ₂ in water

Gaseous Solution

S.No.	Solute	Solvent	Types of solution	Examples
1.	Solid	Gas	Solid in gas	Iodine vapours in air.
2.	Liquid	Gas	Liquid in gas	Water vapours in air.
3.	Gas	Gas	Gas in gas	Air (O ₂ + N ₂)

2.2 Give an example of a solid solution in which the solute is gas.

Ans. Solution of hydrogen in palladium.

2.3 Define the following terms:

(i) Mole fraction

(ii) Molality

(iii) Molarity

(iv) Mass percentage

Ans. (i) **Mole fraction:** It is the ratio of number of moles of a particular component to the total number of moles of all the components.

Example: Mole fraction of component A

$$x_A = \frac{x_A}{x_A + x_B}$$

where x_A is the number of moles of component 'A' and x_B is the number of moles of component B.

(ii) **Molality:** Molality of a solution is defined as the number of moles of the solute dissolved in 1000 g (1 Kg) of the solvent. It is denoted as 'm'.

$$\text{Molality}(m) = \frac{\text{Moles of solute}}{\text{Mass of solvent in Kg}}$$

For example, 1.00 mol Kg⁻¹ (or 1.00 m) solution of KCl means that 1 mol of KCl dissolved in 1 Kg of water.

- (iii) **Molarity:** Molarity (M) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

- (iv) **Mass percentage:** The mass percentage of a component of a solution is defined as:

Mass % of a component

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

- 2.4** Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL^{-1} ?

Ans. Consider 1L (= 1000 mL) of concentrated nitric acid.

Given that density of conc. nitric acid = 1.504 g mL^{-1}

Mass of 1 L of conc. nitric acid = $1000 \text{ mL} \times 1.504 \text{ g mL}^{-1} = 1504 \text{ g}$

Given that concentration of nitric acid (68% by mass).

Mass of nitric acid in 1 L conc. nitric acid = $\frac{68 \times 1504}{100} \text{ g}$

Molar mass of nitric acid (HNO_3) = $(1 + 14 + 48) = 63 \text{ g mol}^{-1}$

Number of moles of HNO_3 in 1L conc. nitric acid

$$= \frac{\text{mass}}{\text{molar mass}} = \frac{68 \times 1504}{100 \times 63} = 16.23 \text{ mol.}$$

Since conc. nitric acid contains 16.23 mol of HNO_3 in 1 L volume, its molarity = 16.23 mol L^{-1} .

- 2.5** A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of solution is 1.2 g mL^{-1} , then what shall be the molarity of the solution?

Ans. (i) **Molality**

Consider 100 g solution. It contains 10 g glucose in 90 g water

Molar mass of glucose $\text{C}_6\text{H}_{12}\text{O}_6 = (6 \times 12 + 12 \times 1 + 6 \times 16) = 180 \text{ g mol}^{-1}$

$$10 \text{ g glucose} = \frac{10}{180} \text{ mol} = 0.0555 \text{ mol}$$

$$90 \text{ g water} = \frac{90}{1000} \text{ kg} = 0.090 \text{ kg water}$$

$$\text{Molality} = \frac{0.0555 \text{ mol}}{0.090 \text{ kg}} = 0.617 \text{ kg}^{-1}$$

(ii) **Mole fractions**

$$\text{Molar mass of H}_2\text{O} = 2 + 16 = 18 \text{ g mol}^{-1}$$

$$90 \text{ g H}_2\text{O} = \frac{90}{18} = 5 \text{ mol.}$$

Total moles of glucose and water

$$= 0.0555 + 5 = 5.0555 \text{ mol}$$

Mole fraction of glucose in the solution

$$= \frac{\text{Moles of glucose}}{\text{Total moles}}$$

$$= \frac{0.0555}{5.0555} = 0.01.$$

$$\text{Mole fraction of water} = 1 - 0.01 = 0.99.$$

(iii) **Molarity of solution**

$$\text{Mass of solution} = 100 \text{ g}$$

$$\text{Density} = 1.2 \text{ g mL}^{-1}$$

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{100 \text{ g}}{1.2 \text{ g mL}^{-1}} = 83.33 \text{ mL.}$$

$$\therefore \text{Moles of glucose in 83.33 mL solution} = 0.0555 \text{ mol}$$

$$\text{Molarity} = \text{Moles of glucose in 1000 mL (1L) solution}$$

$$= \frac{0.0555 \times 1000}{83.33} = 0.67 \text{ mol L}^{-1}.$$

2.6 How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and NaHCO_3 containing equimolar amounts of both?

Ans. (i) **Composition of mixture**

$$\text{Total mass of mixture} = 1 \text{ g}$$

$$\text{Let the mass of Na}_2\text{CO}_3 \text{ in mixture be } x \text{ g}$$

$$\therefore \text{Mass of NaHCO}_3 \text{ in the mixture} = (1 - x) \text{ g}$$

$$\begin{aligned}\text{Molar mass of Na}_2\text{CO}_3 &= 2 \times 23 + 1 \times 12 + 3 \times 16 \\ &= 106 \text{ g mol}^{-1}\end{aligned}$$

$$\text{Moles of Na}_2\text{CO}_3 = \frac{x}{106} \text{ mol}$$

$$\begin{aligned}\text{Molar mass of NaHCO}_3 &= 1 \times 23 + 1 \times 1 + 1 \times 12 + 3 \times 16 \\ &= 84 \text{ g mol}^{-1}\end{aligned}$$

$$\text{Moles of NaHCO}_3 = \frac{1-x}{84} \text{ mol}$$

Since the mixture contains equimolar amounts of the two,
Number of moles of Na_2CO_3 = Number of moles of NaHCO_3

$$\begin{aligned}\frac{x}{106} &= \frac{1-x}{84} \\ 84x &= 106 - 106x \\ (84 + 106)x &= 106 \\ 190x &= 106\end{aligned}$$

$$\therefore x = \frac{106}{190} = 0.558 \text{ g}$$

\therefore Number of moles of Na_2CO_3

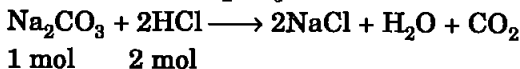
$$= \frac{x}{106} = \frac{0.558 \text{ g}}{106 \text{ g mol}^{-1}} = 0.00526 \text{ mol}$$

Since the mixture is equimolar, number of moles of NaHCO_3

$$= 0.00526.$$

(ii) **Amount of HCl required for reaction**

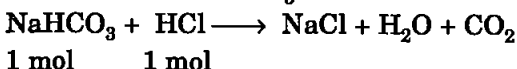
(a) *Reaction with Na_2CO_3*



Since 1 mol Na_2CO_3 reacts with 2 mol of HCl

0.00526 mol Na_2CO_3 would react with $2 \times 0.00526 = 0.01052$ mol.

(b) *Reaction with NaHCO_3*



Since 1 mol NaHCO_3 reacts with 1 mol of HCl

0.00526 mol NaHCO_3 would react with 0.00526 mol HCl.

Total moles of HCl required to react completely with Na_2CO_3 and $\text{NaHCO}_3 = 0.01052 + 0.00526 = 0.01578$ mol.

(iii) Volume of HCl required

Number of moles present = Molarity of solution \times Volume of solution in litre

\therefore Volume of solution (in L) required

$$= \frac{\text{No. of moles of HCl required}}{\text{Molarity of solution}}$$

$$= \frac{0.01578 \text{ mol}}{0.1 \text{ mol L}^{-1}}$$

Volume of solution required in millilitre, mL

$$= \frac{0.01578 \text{ mol} \times 1000 \text{ mL L}^{-1}}{0.1 \text{ mol L}^{-1}} = 157.8 \text{ mL.}$$

2.7 A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

Ans. Mass of 25% solution taken = 300 g

$$\text{Mass of solute in it} = \frac{25 \times 300}{100} = 75 \text{ g}$$

Mass of 40% solution taken = 400 g

$$\text{Mass of solute in it} = \frac{40 \times 400}{100} = 160 \text{ g}$$

Total mass of solute in the final solution = 75 + 160 = 235 g

Total mass of final solution = 300 + 400 = 700 g

$$\therefore \text{Percentage of solute by mass} = \frac{235}{700} \times 100 = 33.6\%$$

Percentage of solvent by mass = 100 - 33.6 = 66.4%

2.8 An antifreeze solution is prepared from 222.6 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1} , then what shall be the molarity of the solution?

Ans. (i) **Calculation of molality**

Mass of solute ethylene glycol = 222.6 g

Molar mass of ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2$

$$= 2 \times 12 + 4 \times 1 + 2 \times 17$$

$$= 62 \text{ g mol}^{-1}.$$

$$\text{Amount (No. of moles) of solute} = \frac{222.6 \text{ g}}{62 \text{ g mol}^{-1}} = 3.59 \text{ mol}$$

Mass of solvent, water = 200 g

Molality = No. of moles of solute dissolved in 1 kg (1000 g) of solvent

$$= \frac{3.59}{200} \times 1000 = 17.95 \text{ mol kg}^{-1}.$$

(ii) **Calculation of molarity**

Total mass of solution = mass of solute + mass of solvent
 $= 222.6 + 200 = 422.6 \text{ g}$

Density of solution = 1.072 g mL^{-1}

$$\therefore \text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}}$$

$$= 394.2 \text{ mL}$$

Molarity = number of moles of solute dissolved in 1L (1000 mL) of solution

$$= \frac{3.59 \text{ mol}}{394.2 \text{ mL}} \times 1000 \text{ mL L}^{-1} = 9.11 \text{ M}.$$

2.9 A sample of drinking water was found to be severely contaminated with chloroform (CHCl_3) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass):

(i) express this in per cent by mass,

(ii) determine the molality of chloroform in the water sample.

Ans. (i) **Calculation of percentage by mass**

Given: Concentration of chloroform = 15 ppm

i.e., 15 parts by mass are present in 10^6 (1 million) parts by mass of solution.

Percentage by mass = number of parts by mass present

$$\text{in 100 parts by mass of solution} = \frac{15 \times 10^2}{10^6} = 15 \times 10^{-4} \%$$

(ii) **Calculation of molality**

Mass of solute in 10^6 g solution = 15 g

Mass of solvent = $10^6 - 15 = 10^6$ g

$$\begin{aligned} \text{Molar mass of solute, chloroform } \text{CHCl}_3 \\ &= 1 \times 12 + 1 + 3 \times 35.5 \\ &= 119.5 \text{ g mol}^{-1} \end{aligned}$$

Moles of solute in 10^6 g solvent

$$= \frac{15 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.125 \text{ mol}$$

Molality = number of moles of solute dissolved in 1 kg
(10^3 g) solvent

$$= \frac{0.125}{10^6} \times 10^3 = 1.25 \times 10^{-4} \text{ m.}$$

2.10 *What role does the molecular interaction play in a solution of alcohol and water?*

Ans. Water and alcohol both have hydrogen bonding. On mixing the two, hydrogen bonding between water and alcohol molecules helps in the dissolution process. However, during dissolution process, the strong association between water molecules due to hydrogen bonding becomes weak and as a result, the solution shows positive deviations from ideal behaviour. The vapour pressure of the solution is higher and the boiling point is lower than expected from ideal behaviour.

2.11 *Why do gases always tend to be less soluble in liquids as the temperature is raised?*

Ans. The dissolution process of any gas in a liquid is exothermic. According to Le Chatelier's Principle on raising the temperature the dissolution equilibrium



shifts in the backward direction which decreases the solubility of the gas.

2.12 *State Henry's law and mention some important applications.*

Ans. **Henry's law:** The solubility of a gas in liquid is directly proportional to the pressure of the gas.

Applications of Henry's law

- (i) In the production of carbonated beverages (as solubility of CO_2 increases at high pressure).
- (ii) In the deep sea diving.

(iii) In the function of lungs.

(iv) For climbers or people living at high altitudes.

2.13 *The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas?*

Ans. Solubility of a gas (ethane) is related to its equilibrium partial pressure by Henry's law

$$m \propto p$$

where m is the mass of gas dissolved in a unit mass of the solvent and p is the equilibrium partial pressure of the gas.

Since the mass of solvent is the same in both the cases

$$\frac{m_1}{m_2} = \frac{p_1}{p_2} \quad \text{or} \quad p_2 = \frac{m_2 p_1}{m_1}$$

Given in the first case $m_1 = 6.56 \times 10^{-3}$ g ; $p_1 = 1$ bar
and in the second case $m_2 = 5.00 \times 10^{-2}$ g

$$p_2 = \frac{5.00 \times 10^{-2} \text{ g} \times 1 \text{ bar}}{6.56 \times 10^{-3} \text{ g}} = 7.62 \text{ bar.}$$

2.14 *What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{\text{mix}}H$ related to positive and negative deviations from Raoult's law?*

Ans. Positive Deviations: In this type of deviation, the partial vapour pressure of each component A and B of solution is higher than the vapour pressure calculated from Raoult's law.

For example: Water and ethanol, chloroform and water.

In case of positive deviation A – B interactions are weaker than those between A – A or B – B. This means that in such solutions molecules of A (or B) will find it easier to escape than in pure state. This will increase the vapour pressure and results in the positive deviation from Raoult's law.

$$\Delta H_{\text{min}} = +\text{Ve}$$

Negative Deviation: In this type of deviation the partial vapour pressure of solution is less than that of ideal solution of same composition. Boiling point of such a solution is relatively higher than the boiling points of both of the components. This type of behaviour is known as negative deviation from Raoult's law.

Here, the intermolecular attractive forces between A – A and B – B are weaker than those between A – B and leads to decrease in vapour pressure.

In case of solutions showing negative deviations, a slight decrease in volume and evolution of heat takes place on mixing.

$$\Delta H_{\text{mix}} = -Ve$$

$$\Delta V_{\text{mix}} = -Ve$$

2.15 *An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?*

Ans. Vapour pressure of water (solvent) at its normal boiling point (100 °C)

$$= p^{\circ} = 1 \text{ atm} = 1.013 \text{ bar}$$

Vapour pressure of solution at the normal boiling point of the solvent (100 °C)

$$= p = 1.004 \text{ bar}$$

\therefore Relative lowering in vapour pressure

$$= \frac{p^{\circ} - p}{p^{\circ}} = x_{\text{solute}} = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$$

where n_1 and n_2 are the number of moles of solvent and solute respectively. If w_1 and w_2 are masses and M_1 and M_2 are the molar masses of the solvent and the solute respectively, then

$$\frac{p^{\circ} - p}{p^{\circ}} = \frac{w_2 M_1}{w_1 M_2}$$

$$p^{\circ} = 1.013 \text{ bar}, p = 1.004 \text{ bar}$$

Mass of solution = 100 g, mass of solute (2%) $w_2 = 2 \text{ g}$

Mass of solvent $w_1 = 100 - 2 = 98 \text{ g}$

Molar mass of solvent (H_2O) = 18 g mol^{-1} . Putting these values

$$\frac{1.013 - 1.004}{1.013} = \frac{2 \text{ g} \times 18 \text{ g mol}^{-1}}{98 \text{ g} \times M_2}$$

$$\text{or} \quad M_2 = \frac{2 \times 18}{98} \times \frac{1.013}{0.009} = 41.35 \text{ g mol}^{-1}.$$

2.16 *Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa*

and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?

Ans. (i) Calculation of mole fractions

Mass of heptane = 26.0 g

Molar mass of heptane (C_7H_{16}) = $7 \times 12 + 16 \times 1 = 100 \text{ g mol}^{-1}$

$$\text{Moles of heptane} = \frac{26.0 \text{ g}}{100 \text{ g mol}^{-1}} = 0.26 \text{ mol.}$$

Mass of octane = 35.0 g

Molar mass of octane (C_8H_{18}) = $8 \times 12 + 18 \times 1 = 114 \text{ g mol}^{-1}$

$$\text{Moles of octane} = \frac{35.0}{114 \text{ g mol}^{-1}} = 0.31 \text{ mol}$$

$$\text{Total moles} = 0.26 + 0.31 = 0.57 \text{ mol}$$

Mole fraction of heptane,

$$x_{\text{heptane}} = \frac{\text{Moles of heptane}}{\text{Total moles}} = \frac{0.26}{0.57} = 0.456$$

Mole fraction of octane, $x_{\text{octane}} = 1 - 0.456 = 0.544$.

(ii) Calculation of vapour pressure

$$p^{\circ}_{\text{heptane}} = 105.2 \text{ kPa}$$

$$x_{\text{heptane}} = 0.456$$

$$\begin{aligned} \text{Partial pressure of heptane } p_{\text{heptane}} &= (p^{\circ} \cdot x)_{\text{heptane}} \\ &= 105.2 \text{ kPa} \times 0.456 = 47.97 \text{ kPa} \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of octane, } p_{\text{octane}} &= (p^{\circ} \cdot x)_{\text{octane}} \\ &= 46.8 \text{ kPa} \times 0.544 = 25.46 \text{ kPa} \end{aligned}$$

$$\begin{aligned} P_{\text{total}} &= P_{\text{heptane}} + P_{\text{octane}} \\ &= 47.97 + 25.46 = 73.43 \text{ kPa.} \end{aligned}$$

2.17 The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

Ans. 1 molal solution = 1 mol solute dissolved in 1000 g of water

Molar mass of water = 18 g mol^{-1}

$$\text{Moles of water} = \frac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.55 \text{ mol}$$

Moles of solute = 1

$$\text{Total moles} = 55.55 + 1 = 56.55$$

$$\begin{aligned} \text{Mole fraction of water in the solution} &= \frac{\text{Moles of water}}{\text{Total moles}} \\ &= \frac{55.55}{56.55} = 0.98 \end{aligned}$$

Since vapour pressure of solution is only due to water (solute being non-volatile).

$$\begin{aligned} p &= p_{\text{H}_2\text{O}}^{\circ} \cdot x_{\text{H}_2\text{O}} = 12.3 \text{ kPa} \times 0.98 \\ &= 12.08 \text{ kPa.} \end{aligned}$$

2.18 Calculate the mass of a non-volatile solute (molar mass 40 g mol⁻¹) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

Ans. Vapour pressure of octane is reduced to 80%. If its vapour pressure from solution = p_s and vapour pressure in pure state is p°

$$p_s = 80\% \text{ of } p^{\circ} = 0.80 p^{\circ}$$

$$\text{Also } p_s = (p^{\circ} \cdot x)_{\text{octane}} \therefore x_{\text{octane}} = \frac{p_s}{p^{\circ}} = \frac{0.80 p^{\circ}}{p^{\circ}} = 0.80$$

$$\text{Mole fraction of solute} = 1 - 0.80 = 0.20$$

$$\text{Molar mass of solute} = 40 \text{ g mol}^{-1}$$

Let its mass be w g

$$\text{Number of moles of solute} = \frac{w}{40} \text{ mol.}$$

$$\text{Molar mass of octane} = (\text{C}_8\text{H}_{18}) = 8 \times 12 + 18 \times 1 = 114 \text{ g mol}^{-1}$$

$$\text{Mass of octane} = 114 \text{ g}$$

$$\text{No. of moles of octane} = \frac{114 \text{ g}}{114 \text{ g mol}^{-1}} = 1 \text{ mol}$$

$$\text{Total moles} = 1 + \frac{w}{40} = \frac{40 + w}{40}$$

$$\text{Mole fraction of solute} = \frac{\frac{w}{40}}{\frac{40 + w}{40}} = \frac{w}{40 + w} = 0.2$$

$$w = 0.2(40 + w) = 8 + 0.2w$$

$$w - 0.2w = 0.8w = 8$$

$$w = \frac{8}{0.8} = 10 \text{ g.}$$

2.19 A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate,

- (i) molar mass of the solute
 (ii) vapour pressure of water at 298 K.

Ans. (i) Applying Raoult's law to I solution

Given: Vapour pressure of solution $p_s = 2.8$ kPa

Mass of water = 90 g

Molar mass of water = 18 g mol^{-1}

$$\text{Moles of water} = n_{\text{H}_2\text{O}} = \frac{90 \text{ g}}{18 \text{ g mol}^{-1}} = 5 \text{ mol.}$$

Let the molar mass of solute = M

Mass of solute = 30 g

$$\text{Moles of solute} = n_{\text{solute}} = \frac{30}{M} \text{ mol.}$$

$$\text{Total moles} = n_{\text{total}} = 5 + \frac{30}{M} = \frac{5M + 30}{M}$$

Mole fraction of water

$$= x_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{total}}} = \frac{5}{(5M + 30)/M} = \frac{5M}{5M + 30}$$

\therefore According to Raoult's law

$$p_s = p_{\text{H}_2\text{O}}^{\circ} \cdot x_{\text{H}_2\text{O}}$$

$$\text{or} \quad 2.8 = p_{\text{H}_2\text{O}}^{\circ} \left(\frac{5M}{5M + 30} \right) \quad \dots(1)$$

(ii) Applying Raoult's law to II solution

Addition of 18 g water increases its moles by 1 to $5 + 1 = 6$ mol

$$\text{Moles of solute} = \frac{30}{M} \text{ mol}$$

$$\text{Total moles} = 6 + \frac{30}{M} = \frac{6M + 30}{M}$$

Mole fraction of water,

$$x_{\text{H}_2\text{O}} = \frac{6}{(6M + 30)/M} = \left(\frac{6M}{6M + 30} \right)$$

Vapour pressure of solution $p_s = 2.9$ kPa

From Raoult's law

$$p_s = p_{\text{H}_2\text{O}}^{\circ} \cdot x_{\text{H}_2\text{O}}$$

$$2.9 = p_{\text{H}_2\text{O}}^{\circ} \frac{6M}{6M + 30} \quad \dots(2)$$

(iii) Calculation of molar mass of solute

Dividing eqn. (2) by eqn. (1)

$$\frac{2.9}{2.8} = p_{\text{H}_2\text{O}}^{\circ} \times \left(\frac{6M}{6M + 30} \right) \times \frac{1}{p_{\text{H}_2\text{O}}^{\circ}} \left(\frac{5M + 30}{5M} \right)$$

$$= \frac{6M(5M + 30)}{5M(6M + 30)} = \frac{30M + 180}{30M + 150}$$

$$2.9(30M + 150) = 2.8(30M + 180)$$

$$87M + 435 = 84M + 504$$

$$(87 - 84)M = (504 - 435)$$

$$3M = 69$$

$$M = 23 \text{ g mol}^{-1}.$$

(iv) Calculation of vapour pressure of water at 298 K

Putting $M = 23 \text{ g mol}$ in eqn. (1)

$$2.8 = p_{\text{H}_2\text{O}}^{\circ} \frac{5 \times 23}{5 \times 23 + 30} = \frac{115}{145} \cdot p_{\text{H}_2\text{O}}^{\circ}$$

or
$$p_{\text{H}_2\text{O}}^{\circ} = \frac{2.8 \times 145}{115} = 3.53 \text{ kPa.}$$

2.20 A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K.

Ans. (i) Calculation of molality of solutions

(a) Molality of cane sugar solution

Molar mass of cane sugar

$$\text{C}_{12}\text{H}_{22}\text{O}_{11} = 12 \times 12 + 22 \times 1 + 11 \times 16$$

$$= 342 \text{ g mol}^{-1}$$

Mass of cane sugar = 5 g

Moles of cane sugar = $\frac{5}{342}$, dissolved in

$$100 - 5 = 95 \text{ g water}$$

$$\therefore \text{Molality of cane sugar solution} = m_1 = \frac{5}{342} \times \frac{1000}{95}$$

(b) *Molality of glucose solution*

Molar mass of glucose,

$$\begin{aligned} \text{C}_6\text{H}_{12}\text{O}_6 &= 6 \times 12 + 12 \times 1 + 6 \times 16 \\ &= 180 \text{ g mol}^{-1} \end{aligned}$$

Mass of glucose = 5 g

Moles of glucose = $\frac{5}{180}$, dissolved in

$$100 - 5 = 95 \text{ g water}$$

$$\therefore \text{Molality of glucose solution} = m_2 = \frac{5}{180} \times \frac{1000}{95}$$

(ii) **Calculation of freezing point of glucose solution**

(a) *Cane sugar solution*

Freezing point = 271 K

Freezing point of water = 273.15 K

$$(\Delta T_f)_1 = 273.15 - 271 = 2.15 \text{ K}$$

$$(\Delta T_f)_1 = K_f \times m_1 \quad \dots(1)$$

(b) *Glucose solution*

Let the depression in freezing point be $(\Delta T_f)_2$. Then

$$(\Delta T_f)_2 = K_f \times m_2 \quad \dots(2)$$

Dividing eqn. (2) by eqn. (1)

$$\left(\frac{(\Delta T_f)_2}{(\Delta T_f)_1} \right) = \frac{K_f \times m_2}{K_f \times m_1} = \frac{m_2}{m_1}$$

Putting values of $(\Delta T_f)_1$, m_1 and m_2 calculated earlier

$$\frac{(\Delta T_f)_2}{2.15 \text{ K}} = \left(\frac{5 \times 1000}{180 \times 95} \right) \times \left(\frac{342 \times 95}{5 \times 1000} \right) = \frac{342}{180}$$

$$\therefore (\Delta T_f)_2 = \frac{2.15 \times 342}{180} = 4.08 \text{ K}$$

Freezing point of solution = 273.15 - 4.08 = 269.07 K.

2.21 Two elements A and B form compounds having formula AB_2 and AB_4 . When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. Calculate atomic masses of A and B.

Ans. Let atomic masses of the elements A and B be a and b respectively.

Molar mass of $AB_2 = M_{AB_2} = (a + 2b)$

Molar mass of $AB_4 = M_{AB_4} = (a + 4b)$

Molar mass M is related to the depression in freezing point as:

$$M = \frac{1000 \times K_f \cdot w_B}{\Delta T_f \cdot w_A}$$

where K_f is molal depression constant of water = $5.1 \text{ K kg mol}^{-1}$

w_B = mass of solute = 1.0 g in both cases

w_A = mass of benzene = 20 g in both cases

ΔT_f = Depression in freezing point

= 2.3 K for AB_2 = 1.3 K for AB_4

Applying the formula to both solutes,

(i) For AB_2

$$M_{AB_2} = (a + 2b) = \frac{1000 \times 5.1 \times 1.0}{2.3 \times 20} = 110.87$$

(ii) For AB_4

$$M_{AB_4} = (a + 4b) = \frac{1000 \times 5.1 \times 1.0}{1.3 \times 20} = 196.15$$

$$a + 4b = 196.15 \quad \dots(i)$$

$$a + 2b = 110.87 \quad \dots(ii)$$

Subtracting (ii) from (i)

$$2b = 85.28 \text{ or } b = 42.64 \text{ g mol}^{-1}$$

Putting in (ii)

$$a + 2 \times 42.64 = 110.87$$

$$a = 110.87 - 85.28 = 25.59 \text{ g mol}^{-1}$$

\therefore Atomic mass of the element A = 25.59 u .

and that of element B = 42.64 u .

2.22 At 300 K , 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar . If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?

Ans. $\pi = CRT$

At constant temperature

$$\frac{\pi_1}{\pi_2} = \frac{C_1}{C_2} \quad \text{or} \quad C_2 = \frac{C_1 \pi_2}{\pi_1}$$

Given when $C_1 = 36 \text{ g L}^{-1}$
 $\pi_1 = 4.98 \text{ bar}$ $\pi_2 = 1.52 \text{ bar}$, $c_2 = ?$

$$C_2 = \frac{(36 \text{ g L}^{-1}) \times (1.52 \text{ bar})}{(4.98 \text{ bar})} = 10.99 \text{ g L}^{-1}$$

In terms of molarity,

$$10.99 \text{ g L}^{-1} = \frac{10.99 \text{ g L}^{-1}}{180 \text{ g mol}^{-1}} = 0.061 \text{ mol L}^{-1}$$

$\therefore C_2 = 0.061 \text{ M.}$

2.23 Suggest the most important type of intermolecular attractive interaction in the following pairs:

- (i) *n*-hexane and *n*-octane
- (ii) I_2 and CCl_4
- (iii) NaClO_4 and water
- (iv) methanol and acetone
- (v) acetonitrile (CH_3CN) and acetone ($\text{C}_3\text{H}_6\text{O}$).

Ans. (i) ***n*-Hexane and *n*-octane**

Both are non-polar covalent, therefore, interaction would be London forces, also known as dispersion forces and instantaneous dipole-induced dipole interactions.

(ii) **I_2 and CCl_4**

Both are non-polar covalent in nature, therefore, London forces.

(iii) **NaClO_4 and water**

NaClO_4 being ionic compound would furnish Na^+ and ClO_4^- ions in the solution. Water is a polar covalent compound. Therefore, the most important interactions would be ion-dipole interactions.

(iv) **Methanol and acetone**

Both are polar covalent compounds, therefore, the most important interactions would be dipole-dipole interactions.

(v) **Acetonitrile (CH_3CN) and acetone (CH_3COCH_3)**

Both are polar covalent compounds, therefore, the most important interactions would be dipole-dipole interactions.

2.24 Based on solute-solvent interactions, arrange the following in order of increasing solubility in *n*-octane and explain. Cyclohexane, KCl, CH₃OH, CH₃CN.

Ans. The solvent *n*-octane is non-polar. According to the rule 'like dissolves like', non-polar solutes will dissolve more readily than a polar solute. Therefore, increasing order of solubility will be the arrangement of solutes in the decreasing order of polar nature which is



2.25 Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?

(i) phenol

(ii) toluene

(iii) formic acid

(iv) ethylene glycol

(v) chloroform

(vi) pentanol.

Ans. (i) **Phenol.** Partially soluble (because it has polar -OH group (which can form hydrogen bonding with water) and non-polar aromatic phenyl group).

(ii) **Toluene.** Insoluble (because it is non-polar).

(iii) **Formic acid.** Highly soluble (because it can form hydrogen bonds with water and dissociate).

(iv) **Ethylene glycol.** Highly soluble (because -OH groups in it can form hydrogen bonds with water).

(v) **Chloroform.** Insoluble (because it cannot form hydrogen bonds with water)

(vi) **Pentanol.** Partially soluble because it has polar -OH group (which can form hydrogen bonds with water) and non-polar C₅H₁₁ group.

2.26 If the density of some lake water is 1.25 g mL⁻¹ and contains 92 g of Na⁺ ions per kg of water, calculate the molality of Na⁺ ions in the lake.

Ans. 1 kg water contains 92 g Na⁺ ions

∴ Molar mass of Na⁺ ions = 23 g mol⁻¹

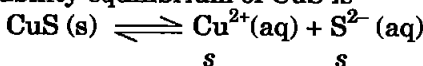
∴ Moles of Na⁺ dissolved per kg of water

$$= \text{molality} = \frac{92 \text{ g kg}^{-1}}{23 \text{ g mol}^{-1}} = 4 \text{ mol kg}^{-1}.$$

2.27 If the solubility product of CuS is 6×10^{-16} , calculate the maximum molarity of CuS in aqueous solution.

Ans. Maximum molarity of CuS = Solubility of CuS in mol L⁻¹

The solubility equilibrium of CuS is



Equilibrium concentrations

where 's' is the solubility of CuS in mol L⁻¹

$$K_{sp} = [\text{Cu}^{2+}] [\text{S}^{2-}] = s \times s = s^2$$

or

$$s = \sqrt{K_{sp}}$$

Given,

$$K_{sp} = 6 \times 10^{-16}$$

$$s = \sqrt{6 \times 10^{-16}} = 2.45 \times 10^{-8} \text{ mol L}^{-1}.$$

- 2.28** Calculate the mass percentage of aspirin (C₉H₈O₄) in acetonitrile (CH₃CN) when 6.5 g of C₉H₈O₄ is dissolved in 450 g of CH₃CN.

Ans. Mass of aspirin (solute) = 6.5 g

Mass of acetonitrile (solvent) = 450 g

Total mass of solution = 450 + 6.5 = 456.5 g

$$\begin{aligned} \text{Mass per cent of aspirin} &= \frac{\text{Mass of aspirin}}{\text{Mass of solution}} \times 100 \\ &= \frac{6.5 \times 100}{456.5} = 1.424\%. \end{aligned}$$

- 2.29** Nalorphene (C₁₉H₂₁NO₃), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of 1.5 × 10⁻³ m aqueous solution required for the above dose.

Ans. Molality of solution = 1.5 × 10⁻³ m

$$= 1.5 \times 10^{-3} \text{ mol kg}^{-1}$$

Molar mass of nalorphene (C₁₉H₂₂NO₃)

$$\begin{aligned} &= 19 \times 12 + 22 \times 1 + 1 \times 14 + 3 \times 16 \\ &= 312 \text{ g mol}^{-1}. \end{aligned}$$

1.5 × 10⁻³ mol of nalorphene

$$\begin{aligned} &= 1.5 \times 10^{-3} \text{ mol} \times 312 \text{ g mol}^{-1} \\ &= 0.468 \text{ g} = 468 \text{ mg}. \end{aligned}$$

Mass of solvent = 1 kg = 1000 g

Total mass of solution = 1000 g + 0.468 g = 1000.468 g

For 468 mg of nalorphene, the mass of 1.5 × 10⁻³ m solution required

$$= 1000.468 \text{ g}$$

For 1.5 mg of nalorphene. The mass of the solution required

$$= \frac{1.5 \times 1000.468}{468} = 3.21 \text{ g.}$$

2.30 Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol.

Ans. Molarity of solution to be prepared = 0.15 M = 0.15 mol L^{-1}

Volume of solution to be prepared = 250 mL

Molar mass of solute, benzoic acid C_6H_5COOH

$$= (6 \times 12 + 5 \times 1 + 12 + 2 \times 16 + 1) = 122 \text{ g mol}^{-1}.$$

The number of moles of benzoic acid required:

(i) For preparing 1 L or 1000 mL of 0.15 M solution = 0.15 mol.

(ii) For preparing 250 mL of 0.15 M solution

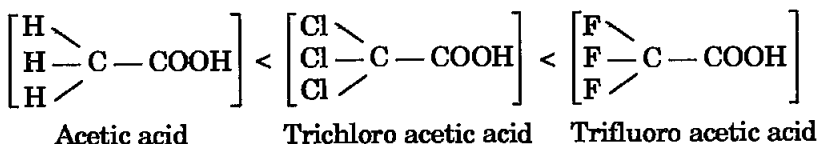
$$= \frac{0.15 \times 250}{1000} = \frac{0.15}{4} \text{ mol}$$

Mass of benzoic acid required

$$= \left(\frac{0.15}{4} \text{ mol} \right) (122 \text{ g mol}^{-1}) = 4.575 \text{ g.}$$

2.31 The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

Ans. The depression in freezing point increases in the order:



It is because the presence of more electronegative group with more electron withdrawing power on the carbon atom adjacent to $-\text{COOH}$ group help in release of H^+ ions and makes the acid stronger. Fluorine is the most electronegative element with maximum electron withdrawing inductive effect. Hence trifluoroacetic acid is the strongest with maximum ionisation (α , degree of ionisation is the highest) followed by Cl in trichloroacetic acid and H in acetic acid. More the number of ions produced, more is the depression

in freezing point, hence the given order of depression in freezing point produced by the three.

- 2.32** Calculate the depression in the freezing point of water when 10 g of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86 \text{ K kg mol}^{-1}$.

Ans. (i) Calculation of molality of solution

Mass of solute dissolved = 10 g

$$\begin{aligned} \text{Molar mass of solute, } \text{CH}_3\text{CH}_2\text{CHClCOOH or } (\text{C}_4\text{H}_7\text{O}_2\text{Cl}) \\ &= 4 \times 12 + 7 \times 1 + 2 \times 16 + 1 \times 35.5 \\ &= 122.5 \text{ g mol}^{-1} \end{aligned}$$

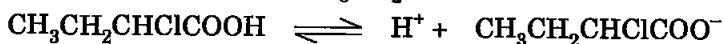
$$\begin{aligned} \text{Number of moles of solute dissolved } (n) &= \frac{10 \text{ g}}{122.5 \text{ g mol}^{-1}} \\ &= 8.16 \times 10^{-2} \text{ mol} \end{aligned}$$

Mass of solvent = 250 g

$$\begin{aligned} \text{Molality of solution} &= \frac{8.16 \times 10^{-2} \text{ mol} \times 1000 \text{ g mol}^{-1}}{250 \text{ g}} \\ &= 0.3264 \text{ mol kg}^{-1} \end{aligned}$$

Effect of dissociation

Dissociation process of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$ is



Initial moles	n	0	0
Equilibrium moles	$n(1 - \alpha)$	$n\alpha$	$n\alpha$

$$\begin{aligned} \text{Total moles at equilibrium} &= n(1 - \alpha) + 2n\alpha \\ &= n(1 + \alpha) \end{aligned}$$

and $\alpha = \sqrt{\frac{K_a}{C}}$, $K_a = 1.4 \times 10^{-3}$

In dilute solutions, the molarity is nearly same as molality.

$$\alpha = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$$

$$i = \frac{1 + \alpha}{1} = 1 + 0.065 = 1.065.$$

(ii) Calculation of depression in freezing point

$$\begin{aligned} \Delta T_f &= i K_f m = (1.065) (1.86 \text{ K kg mol}^{-1}) (0.3264 \text{ mol kg}^{-1}) \\ &= 0.65 \text{ K} = 0.65^\circ \text{C}. \end{aligned}$$

2.33 19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0°C . Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

Ans. (i) **Calculation of observed molar mass of solute $(M_2)_{\text{obs}}$**

Mass of solvent, $w_1 = 500$ g

Mass of solute, $w_2 = 19.5$ g

$K_f = 1.86$ K kg mol $^{-1}$

$\Delta T_f = 1.0^\circ\text{C} = 1.0$ K

$$\begin{aligned}(M_2)_{\text{obs}} &= \frac{1000 K_f w_2}{w_1 \Delta T_f} \\ &= \frac{(1000 \text{ g kg}^{-1})(1.86 \text{ K kg mol}^{-1})(19.5 \text{ g})}{(500 \text{ g})(1.0 \text{ K})} \\ &= 72.54 \text{ g mol}^{-1}\end{aligned}$$

(ii) **Calculated molar mass $(M_2)_{\text{cal}}$**

Formula of solute $\text{CH}_2\text{FCOOH} = \text{C}_2\text{H}_3\text{O}_2\text{F}$

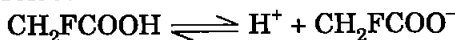
Calculated molar mass, $(M_2)_{\text{cal}}$

$$\begin{aligned}&= 2 \times 12 + 3 \times 1 + 2 \times 16 + 1 \times 19 \\ &= 24 + 3 + 32 + 19 = 78 \text{ g mol}^{-1}\end{aligned}$$

(iii) **Calculation of van't Hoff factor i and degree of dissociation α**

$$i = \frac{(M_2)_{\text{cal}}}{(M_2)_{\text{obs}}} = \frac{78}{72.54} = 1.0753$$

For dissociation of solute



Initial concentration	c	0	0
Equilibrium concentration	$c(1 - \alpha)$	$c\alpha$	$c\alpha$

Total concentration = $c(1 - \alpha + \alpha + \alpha) = c(1 + \alpha)$

$$\begin{aligned}i &= \frac{\text{Actual concentration}}{\text{Expected concentration}} = \frac{c(1 + \alpha)}{c} \\ &= 1 + \alpha\end{aligned}$$

$$\alpha = i - 1 = 1.0753 - 1 = 0.0753$$

(iv) **Dissociation constant of the acid**

From dissociation process

$$K_a = \frac{[\text{H}^+][\text{CH}_2\text{FCOO}^-]}{[\text{CH}_2\text{FCOOH}]}$$

$$\frac{(c\alpha) \times (c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

Since α is very small, $(1-\alpha) \simeq 1$

$$K_a = c\alpha^2$$

$$\text{Molar concentration, } c = \frac{w_2 \times 1000}{M_2 \times V}$$

V = volume of solution = volume of water

Taking density of water as 1 g mL^{-1}

$$V = (500 \text{ g}) / (1 \text{ g mL}^{-1}) = 500 \text{ mL}$$

$$\therefore c = \frac{(19.5 \text{ g}) \times (1000 \text{ mL L}^{-1})}{(78 \text{ g mol}^{-1})(500 \text{ mL})} = 0.5 \text{ M}$$

$$K_a = c\alpha^2 \\ = 0.5 \times (0.0753)^2 = 2.835 \times 10^{-3}$$

2.34 Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water.

Ans. (i) Calculation of mole fractions

Mass of water = 450 g

Molar mass of water = 18 g mol^{-1}

$$\text{Number of moles of water} = n_1 = \frac{450}{18} = 25 \text{ mol}$$

Mass of glucose = 25 g.

Molar mass of glucose,

$$\begin{aligned} \text{C}_6\text{H}_{12}\text{O}_6 &= 6 \times 12 + 12 \times 1 + 6 \times 16 \\ &= 72 + 12 + 96 = 180 \text{ g mol}^{-1} \end{aligned}$$

Number of moles of glucose

$$= n_2 = \frac{25 \text{ g}}{180 \text{ g mol}^{-1}} = 0.139 \text{ mol}$$

Mole fraction of water x_1

$$= \frac{n_1}{n_1 + n_2} = \frac{25}{25 + 0.139} = \frac{25}{25.139} = 0.9945$$

(ii) Calculation of vapour pressure

Vapour pressure of pure water, $p^0 = 17.535 \text{ mm Hg}$

Mole fraction of water in the solution = $x = 0.9945$

$$\begin{aligned} \therefore \text{Vapour pressure of water from solution} &= p^\circ \cdot x \\ &= 17.535 \times 0.9945 = 17.44 \text{ mm Hg.} \end{aligned}$$

2.35 Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

Ans. According to Henry's law, $p = K_H x$

Given: pressure of methane, $p = 760$ mm Hg

Henry's law constant = $K_H = 4.27 \times 10^5$ mm Hg

Mole fraction of methane in the solution

$$\begin{aligned} &= \text{solubility} = x = \frac{p}{K_H} \\ &= \frac{760 \text{ mm Hg}}{4.27 \times 10^5 \text{ mm Hg}} = 1.78 \times 10^{-3} = 178 \times 10^{-5} \end{aligned}$$

2.36 100 g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}). The vapour pressure of pure liquid B was found to be 500 Torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 Torr.

Ans. (i) **Calculation of mole fractions**

Mass of liquid A = 100 g

Molar mass of liquid A = 140 g mol^{-1}

$$\text{Number of moles of A} = n_A = \frac{100 \text{ g}}{140 \text{ g mol}^{-1}} = 0.714$$

Mass of liquid B = 1000 g

Molar mass of liquid B = 180 g mol^{-1}

$$\text{Number of moles of liquid B} = n_B = \frac{1000}{180} = 5.555 \text{ mol}$$

$$\text{Total number of moles} = n_A + n_B = 5.555 + 0.714 = 6.269$$

$$\text{Mole fraction of liquid A} = x_A = \frac{n_A}{n_A + n_B} = \frac{0.714}{6.269} = 0.114$$

$$\text{Mole fraction of liquid B} = x_B = 1 - x_A = 1 - 0.114 = 0.886$$

(ii) **Calculation of vapour pressure of pure A**

Given: vapour pressure of pure B = $p_B^\circ = 500$ Torr

$$\begin{aligned} p &= p_A + p_B \text{ vapour pressure of solution} = p = 475 \text{ Torr} \\ &= p_A^\circ \cdot x_A + p_B^\circ \cdot x_B \end{aligned}$$

$$475 \text{ Torr} = p_A^\circ \times 0.114 + 500 \times 0.886$$

$$= 0.114 p_A^\circ + 443 \text{ Torr}$$

$$0.114 p_A^\circ = 475 - 443 = 32 \text{ Torr}$$

$$p_A^\circ = \frac{32 \text{ Torr}}{0.114} = 280.7 \text{ Torr.}$$

(iii) Vapour pressure of liquid A from solution

$$p_A = p_A^\circ x_A$$

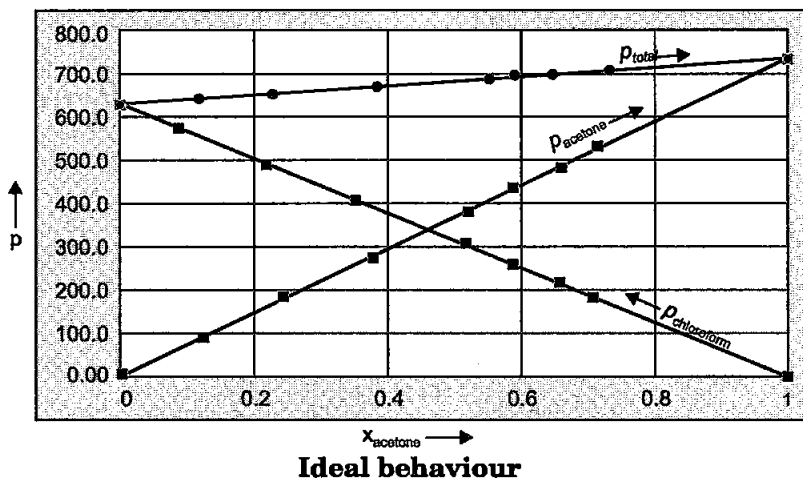
$$= 280.7 \text{ Torr} \times 0.114 = 32 \text{ Torr.}$$

2.37 Vapour pressures of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total} , $p_{\text{chloroform}}$, and p_{acetone} as a function of x_{acetone} . The experimental data observed for different compositions of mixture is:

$100 \times x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8
	58.2	64.5	72.1		
p_{acetone} /mm Hg	0	54.9	110.1	202.4	322.7
	405.9	454.1	521.1		
$p_{\text{chloroform}}$ /mm Hg	632.8	548.1	469.4	359.7	257.7
	193.6	161.2	120.7		

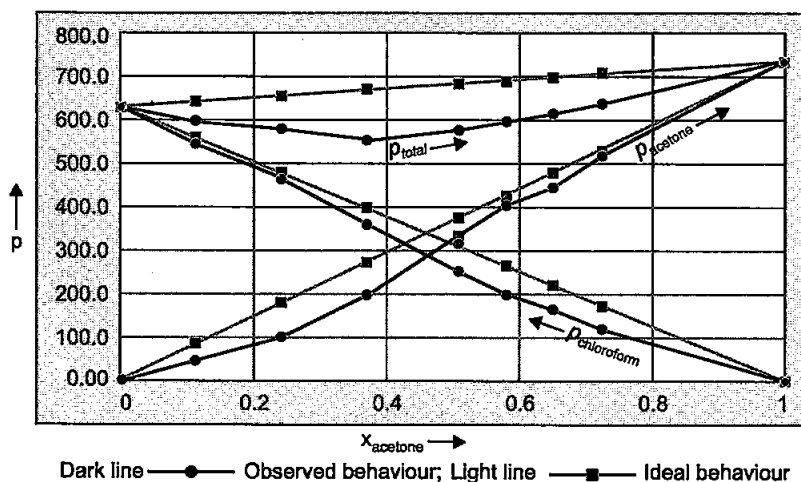
Plot this data also on the same graph paper, indicate whether it has positive deviation or negative deviation from the ideal solution.

Ans.



From the given data, p_{total} can be calculated for various compositions as shown below.

x_{acetone}	0.00	0.118	0.234	0.360	0.508
	0.582	0.645	0.721		
$p_{\text{acetone}}/\text{mm Hg}$	0.00	54.9	110.1	202.4	322.7
	405.9	454.1	521.1		
$p_{\text{chloroform}}/\text{mm Hg}$	632.8	548.1	469.4	359.7	257.7
	193.6	161.2	120.7		
$p_{\text{total}}/\text{mm Hg}$	632.8	603.0	579.5	562.1	580.4
	599.5	615.3	641.8		



Observed behaviour

As curve for p_{total} vs x_{acetone} is not straight line and has a minima, the system shows negative deviation.

2.38 Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of toluene.

Ans. (i) **Calculation of mole fractions of benzene and toluene in the solution**

Given: Mass of benzene = 80 g

Molar mass of benzene C_6H_6

$$= 6 \times 12 + 6 \times 1 = 72 + 6 = 78 \text{ g mol}^{-1}$$

∴ Number of moles of benzene

$$= \frac{80 \text{ g}}{78 \text{ g mol}^{-1}} = 1.026 \text{ mol}$$

Mass of toluene = 100 g

Molar mass of toluene,

$$\begin{aligned} \text{C}_6\text{H}_5\text{CH}_3 &= 6 \times 12 + 5 \times 1 + 1 \times 12 + 3 \times 1 \\ &= 72 + 5 + 12 + 3 = 92 \text{ g mol}^{-1} \end{aligned}$$

Number of moles of toluene

$$= \frac{100 \text{ g}}{92 \text{ g mol}^{-1}} = 1.087 \text{ mol}$$

Mole fraction of benzene

$$= \frac{n_{\text{benzene}}}{n_{\text{benzene}} + n_{\text{toluene}}} = \frac{1.026}{1.026 + 1.087} = 0.486$$

Mole fraction of toluene = $1 - x_{\text{benzene}} = 1 - 0.486 = 0.514$

(ii) **Calculation of vapour pressures**

According to Raoult's law $p_i = p_i^\circ \times x_i$

$$\begin{aligned} \text{Vapour pressure of benzene} &= p_{\text{benzene}} = p_{\text{benzene}}^\circ \times x_{\text{benzene}} \\ &= (50.71 \text{ mm Hg}) \times (0.486) = 24.65 \text{ mm Hg} \end{aligned}$$

$$\begin{aligned} \text{Vapour pressure of toluene} &= p_{\text{toluene}} = p_{\text{toluene}}^\circ \times x_{\text{toluene}} \\ &= (32.06 \text{ mm Hg}) \times (0.514) = 16.48 \text{ mm Hg} \end{aligned}$$

Total vapour pressure

$$p_{\text{total}} = 24.65 + 16.48 = 41.13 \text{ mm Hg.}$$

(iii) **Calculation of mole fraction of benzene in vapour phase**

Mole fraction of benzene in vapour phase

$$\begin{aligned} &= \frac{\text{Vapour pressure of benzene}}{\text{Total vapour pressure}} \\ &= \frac{24.65 \text{ mm Hg}}{41.13 \text{ mm Hg}} = 0.60. \end{aligned}$$

2.39 *The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K, if the Henry's law constants for oxygen and nitrogen are $3.30 \times 10^7 \text{ mm}$ and $6.51 \times 10^7 \text{ mm}$ respectively, calculate the composition of these gases in water.*

Ans. (i) **Calculation of partial pressure of O_2 and N_2**

Total pressure of air = 10 atm

Since O_2 is present 20% by volume and N_2 79%

$$\text{Partial pressure of } O_2 = p_{O_2} = \frac{10 \times 20}{100} = 2 \text{ atm}$$

$$\text{Partial pressure of } N_2 = p_{N_2} = \frac{10 \times 79}{100} = 7.9 \text{ atm}$$

(ii) **Calculation of mole fractions of O_2 and N_2**

According to Henry's law

$$p = K_H \cdot x$$

$$\therefore x = \frac{p}{K_H}$$

(a) K_H for $O_2 = 3.30 \times 10^7 \text{ mm Hg}$

$$\begin{aligned} \text{Partial pressure of } O_2 &= 2 \text{ atm} = 2 \text{ atm} \times 760 \text{ mm Hg atm}^{-1} \\ &= 1520 \text{ mm Hg} \end{aligned}$$

Mole fraction of O_2

$$= x_{O_2} = \frac{1520 \text{ mm Hg}}{3.30 \times 10^7 \text{ mm Hg}} = 4.61 \times 10^{-5}$$

(b) K_H for $N_2 = 6.51 \times 10^7 \text{ mm Hg}$

$$\begin{aligned} \text{Partial pressure of } N_2 &= 7.9 \text{ atm} = 7.9 \text{ atm} \times 760 \text{ mm Hg atm}^{-1} \\ &= 6004 \text{ mm Hg} \end{aligned}$$

$$\text{Mole fraction of } N_2, x_{N_2} = \frac{6004 \text{ mm Hg}}{6.51 \times 10^7 \text{ mm Hg}} = 9.22 \times 10^{-5}$$

2.40 Determine the amount of $CaCl_2$ ($i = 2.47$) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at $27^\circ C$.

Ans.

$$\pi = iCRT$$

$$C = \frac{n}{V}$$

$$\therefore \pi = i = \frac{nRT}{V}$$

$$\text{Amount of solute} = n = \frac{\pi V}{iRT}$$

Given: $\pi = 0.75 \text{ atm}$

$$T = 27 + 273 = 300 \text{ K}$$

$$V = 2.5 \text{ L}$$

$$R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$i = 2.47$$

Putting these values in the above expression

$$n = \frac{(0.75 \text{ atm})(2.5 \text{ L})}{(2.47)(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})}$$

$$= 0.03 \text{ mol.}$$

2.41 Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25 °C, assuming that it is completely dissociated.

Ans.

$$\pi = iCRT$$

$$C = \frac{n}{V} = \frac{w}{MV}$$

$$\pi = \frac{iwRT}{MV}$$

Given: Mass of solute, $w = 25 \text{ mg} = 0.025 \text{ g}$

Volume of solution = $V = 2 \text{ L}$

Temperature $T = 25 + 273 = 298 \text{ K}$

$R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$

Molar mass of $\text{K}_2\text{SO}_4 = M = 2 \times 39 + 1 \times 32 + 4 \times 16$
 $= 174 \text{ g mol}^{-1}$

From dissociation of K_2SO_4 : $\text{K}_2\text{SO}_4 \longrightarrow 2\text{K}^+ + \text{SO}_4^{2-}$; $i = 3$

$$\therefore \pi = \frac{(3)(0.025 \text{ g})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(174 \text{ g mol}^{-1})(2 \text{ L})}$$

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

□□□