

LIQUID SOLUTIONS

Solution: A homogeneous mixture of two or more substances. (Solute + solvent = solution)

Saturated Solution : A solution that is in equilibrium with pure solid solute. No more solute can be dissolved in it.

1. Methods of expressing the concentration of a solution

The concentration of a solution can be expressed in a number of ways. The important methods are:

(i) Mass percentage or per cent by mass:

$$\begin{aligned}
 \%(w/w) \text{ Mass percentage of solute} &= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100 \\
 &= \frac{\text{Mass of solute}}{\text{Mass of solute} + \text{Mass of solvent}} \\
 &= \frac{\text{Mass of solute}}{\text{Volume of solution} \times \text{Density of solution}}
 \end{aligned}$$

(ii) Percent mass by volume:

$$\%(w/v) = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

(iii) Parts per million (ppm) :

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

(iv) Mole fraction:

Let n moles of solute (A) and N moles of solvent (B) be present in a solution.

$$\text{Mole fraction of solute} = \frac{n}{N+n} = X_A, \text{ Mole fraction of solvent} = \frac{N}{N+n} = X_B$$

In binary solution, $X_A + X_B = 1$

Mole fraction is independent of temperature of the solution.

(v) Molality

$$\text{Molality } (m) = \frac{\text{No. of moles of solute}}{\text{weight (in kg) of solvent}}$$

Let w_A grams of the solute of molecular mass m_A be present in w_B grams of the solvent, then

$$\text{Molality } (m) = \frac{w_A}{m_A \times w_B} \times 1000$$

Relation between mole fraction and Molality :

$$\frac{X_A \times 1000}{X_B \times m_B} = m = \frac{w_A \times 1000}{w_B \times m_B}$$

Note: (i) Molality is the most convenient method to express the concentration because it involves the mass of liquids rather than their volumes. It is also independent of the variation in temperature.

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(vi) Molarity (Molar concentration)

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume (in litre) of solution}}$$

$$\text{Molarity of the solution} = \frac{w_A}{m_A \times V} \times 1000$$

Relation between molarity and % solute by mass :

Let d = density of solution in g/mL and let it contains $x\%$ (w/w) solute by mass.

Number of moles of solute in 1 litre

$$= \frac{\text{mass of solute in gram}}{\text{grams molecular mass of solute}} = \frac{x \times d \times 10}{M_{\text{solute}}}$$

$$M = \frac{x \times d \times 10}{m_A}$$

Molarity of dilution:

$$\begin{array}{ccc} \text{Before dilution} & & \text{After dilution} \\ M_1 V_1 & = & M_2 V_2 \end{array}$$

Molarity of mixing:

$$M_1 V_1 + M_2 V_2 + M_3 V_3 = M_R (V_1 + V_2 + V_3) \quad M_R = \text{resultant molarity}$$

Relationship between molality and molarity :

$$\text{Molality (m)} = \frac{\text{molarity}}{d - \text{molarity} \times m_{\text{solute}}} = \frac{1000 \times M}{1000 \times d - M \times M_{\text{solute}}}$$

Illustration 1. The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/mL. Calculate the molarity of the solution.

Solution: In solving such numericals, the following formula can be applied:

$$\text{Molarity} = \frac{\% \text{ strength of soln.} \times \text{density of soln.} \times 10}{\text{Mol. mass}}$$

$$M = \frac{13 \times 1.09 \times 10}{98} = 1.445 \text{ M}$$

Illustration 2. The density of a 3 M sodium thiosulphate solution ($\text{Na}_2\text{S}_2\text{O}_3$) is 1.25 g/mL. Calculate (i) the percentage by mass of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate and (iii) molalities of Na^+ and $\text{S}_2\text{O}_3^{2-}$ ions.

Solution: $M = \frac{x \times d \times 10}{m_A} \Rightarrow 3 = \frac{x \times 1.25 \times 10}{158}$

$$\therefore x = 37.92$$

(ii) No. of moles of $\text{Na}_2\text{S}_2\text{O}_3 = \frac{474}{158} = 3$

Mass of water = $(1250 - 474) = 776 \text{ g}$, No. of moles of water = $\frac{776}{18} = 43.1$

Mole fraction of $\text{Na}_2\text{S}_2\text{O}_3 = \frac{3}{43.1 + 3} = \frac{3}{46.1} = 0.065$

(iii) No. of moles of Na^+ ions
 $= 2 \times \text{No. of moles of } \text{Na}_2\text{S}_2\text{O}_3 = 2 \times 3 = 6$

Molality of Na^+ ion = $\frac{\text{No. of moles of } \text{Na}^+ \text{ ions}}{\text{Mass of water in kg}}$

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$$= \frac{6}{776} \times 1000 = 7.73 \text{ m}$$

No. of moles of $\text{S}_2\text{O}_3^{2-}$ ions = No. of moles of $\text{Na}_2\text{S}_2\text{O}_3$

$$\text{Molality of } \text{S}_2\text{O}_3^{2-} \text{ ions} = \frac{3}{776} \times 1000 = 3.86 \text{ m}$$

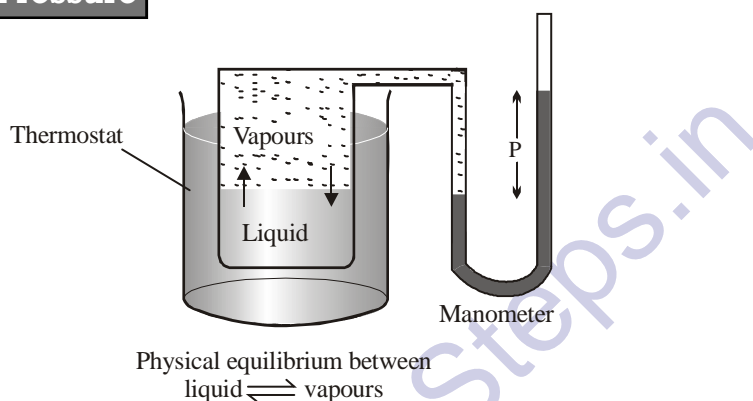
Illustration 3. One litre of sea water weighs 1030 g and contains about $6 \times 10^{-3}\text{g}$ of dissolved O_2 . Calculate the concentration of dissolved oxygen in ppm.

Solution: Mass of O_2 in mg = $6 \times 10^{-3}\text{g} \times 10^3 \text{ mg/g} = 6\text{mg}$

$$\text{ppm of } \text{O}_2 \text{ in 1030 g sea water} = \frac{\text{Mass of } \text{O}_2 \text{ in mg}}{\text{Mass of sea water in kg}} = \frac{6}{(1030/1000)\text{kg}}$$

$$= \frac{6 \times 1000}{1030} = 5.8\text{ppm}$$

2. Vapour Pressure



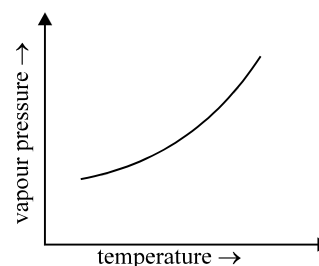
The pressure exerted by the vapour (molecules in the vapour phase) over the surface of the liquid at the equilibrium at given temperature is called the vapour pressure of the liquid.

Factors affecting vapour pressure

(i) Temperature :

Vapour pressure \propto Temperature

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called its **boiling point**.



(ii) Nature of liquid:

Vapour pressure of liquid $\propto \frac{1}{\text{The strength of intermolecular forces acting between molecules}}$

For example, ethyl alcohol has higher vapour pressure because of the weak intermolecular forces acting between its molecules than water which has stronger intermolecular forces acting between water molecules of volatile liquid has lower boiling point than a non-volatile liquid.

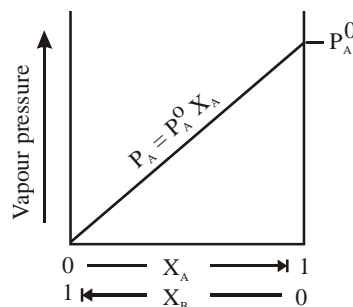
3. Vapour Pressure of solution

(i) Vapour Pressure of a Solution Containing Non Volatile Solute - Raoult's Law :

Raoult's Law : According to this law, the partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.

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$$P_A = P_A^0 X_A \quad \text{.....(1)}$$



Relative Lowering of vapour pressure: For a solution of a non-volatile solute in a liquid, the vapour pressure contribution by the non-volatile solute is negligible. Therefore, the partial vapour pressure of a solution containing a non-volatile solute is equal to the product of vapour pressure of the pure liquid (solvent P_A^0) and its mole fraction in the solution.

Let X_A be the mole fraction of solvent A, then (Here $p_B^0 = \text{negligible as solute is non-volatile}$)

$$P_A = P_A^0 X_A$$

If X_B be the mole fraction of the solute B, then

$$X_A + X_B = 1 \Rightarrow X_A = 1 - X_B$$

hence $P_A = P_A^0 (1 - X_B) = P_A^0 - P_A^0 X_B \Rightarrow P_A^0 X_B = P_A^0 - P_A$ (2)

($P_A^0 - P_A$ is known as lowering of vapour pressure)

$$\frac{P_A^0 - P_A}{P_A^0} = X_B \left(\frac{P_A^0 - P_A}{P_A^0} \text{ is called relative lowering of vapour pressure, (RLVP)} \right) \quad \text{.....(3)}$$

Therefore, Raoult's law states that the relative lowering of vapour pressure $\left(\frac{P_A^0 - P_A}{P_A^0} \right)$, for a non-volatile solute is equal to the mole fraction of the solute when the solvent alone is volatile.

Illustration 4: The vapour pressure of pure water at 37°C is 47.1 torr. What is the vapour pressure of an aqueous solution at 37°C containing 20 g of glucose dissolved in 500 gm of water. Also calculate vapour pressure lowering.

Solution: $n_{\text{H}_2\text{O}} = \frac{500}{18} = 27.78 \text{ mol}$, $n_{(\text{glucose})} = \frac{20}{180} = 0.11 \text{ mol}$

$$X_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{(\text{glucose})}} = \frac{27.78}{27.78 + 0.11} = \frac{27.78}{27.89} = 0.996$$

According to Raoult's law,

Vapour pressure of solution $P_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}^0 X_{\text{H}_2\text{O}} = 47.1 \times 0.996 = 46.9 \text{ torr}$

Lowring of vapour pressure $P_{\text{H}_2\text{O}}^0 - P_{\text{H}_2\text{O}} = 47.1 - 46.9 = 0.2 \text{ torr}$

Illustration 5. The vapour pressure of ethyl alcohol at 25°C is 59.2 torr. The vapour pressure of a solution of urea in ethyl alcohol is 51.3 torr. What is the molality of the solution?

Solution: Given: $P_A^0 = 59.2 \text{ torr}$, $p_A = 51.3 \text{ torr}$

By RLVP $\Rightarrow X_{\text{solute}} = \frac{7.9}{59.2} = .1334$

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$$\square \text{ (molality) } m = \frac{X_B}{X_A} \times \frac{1000}{M_{\text{solvent}}} = \frac{X_B}{(1 - X_B)} \times \frac{1000}{M_{\text{solvent}}} \quad (\square X_A + X_B = 1)$$

$$m = \frac{0.1334}{0.8666} \times \frac{1000}{46} = 3.346 \text{ molal}$$

Illustration 6. Calculate relative lowering of vapour pressure of 0.161 molal aqueous solution.

Solution : we know Molality = $\frac{X_B \times 1000}{(1 - X_B) \times m_{\text{solvent}}} \Rightarrow 0.161 = \frac{X_B \times 1000}{(1 - X_B) \times 18}$

$$X_A = 0.00289 \Rightarrow \text{RLVP} = X_A = 0.00289$$

1. Daily Practice Problem Sheet

- Q.1** The vapour pressure of ether at 20°C is 442 mm. When 7.2 g of a solute is dissolved in 60 g ether, vapour pressure is lowered by 32 units. If molecular weight of ether is 74 then molecular weight of solute is -
 (A) 113.77 (B) 150.35 (C) 116.23 (D) 190.26
- Q.2** The vapour pressure of pure benzene at 25°C is 639.7 mm of Hg and the vapour pressure of a solution of a solute in C₆H₆ at the same temperature is 631.9 mm of Hg. Molality of solution is -
 (A) 0.079 mol/kg of solvent (B) 0.256 mol/kg of solvent
 (C) 0.158 mol/kg of solvent (D) 0.316 mol/kg of solvent
- Q.3** A 6% (by weight) of non-volatile solute in isopentane at 300 K has a vapour pressure of 1426 mm Hg. 20 g of isopentane is now added to the solution. The resulting solution has a vapour pressure of 1445 mm of Hg at the same temperature. Then :
 (i) Molecular weight of solute is -
 (A) 28.32 (B) 92.81 (C) 113.30 (D) 56.65
 (ii) Vapour pressure of isopentane at 300 K is -
 (A) 1541.68 mm (B) 770.89 mm (C) 1212.46 mm (D) 981.32 mm
- Q.4** Find out the weight of solute (M. wt. 60) that is required to dissolve in 180 g water to reduce the vapour pressure to 4/5th of pure water -
 (A) 130 g (B) 150 g (C) 300 g (D) 75 g
- Q.5** The molality of a solution containing a non-volatile solute if the vapour pressure is 2% below the vapour pressure of pure water, will be -
 (A) 2.213 (B) 2.518 (C) 1.133 (D) 1.891
- Q.6** The weight of a non-volatile solute (m. wt. 40). Which should be dissolved in 114 g octane to reduce its vapour pressure to 80%, is -
 (A) 20 gm (B) 10 gm (C) 7.5 gm (D) 5 gm
- Q.7** Twenty gram of a solute are added to 100 g of water at 25°C. The vapour pressure of pure water is 23.76 mm Hg, vapour pressure of solution is 22.41 mm Hg. The mass of this solute that is required in 100 g water to reduce the vapour pressure to one-half of the pure water is -
 (A) 333 g (B) 666 g (C) 166 g (D) 256 g
- Q.8** Vapour pressure of pure water is 40 mm. If a non-volatile solute is added to it vapour pressure falls by 4 mm. Hence, molality of solution is -
 (A) 6.173 molal (B) 3.0864 molal (C) 1.543 molal (D) 0.772 molal
- Q.9** The vapour pressure of pure liquid solvent A is 0.80 atm. When a non-volatile substance B is added to the solvent, its vapour pressure drops to 0.60 atm ; mole fraction of the component B in the solution is
 (A) 0.50 (B) 0.25 (C) 0.75 (D) 0.40

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- Q.10** Vapour pressure of CCl_4 at 25°C is 143 mm Hg. If 0.5 gm of non-volatile solute (mol. mass 65) is dissolved in 100 ml CCl_4 , then the vapour pressure of the solution at 25°C is -
[Given : Density of $\text{CCl}_4 = 1.58 \text{ g/cm}^3$]
(A) 141.93 mm (B) 94.39 mm (C) 199.34 mm (D) 143.99 mm
- Q.11** Lowering of vapour pressure of 1.00 m solution of a non-volatile solute in a hypothetical solvent of molar mass 40 g at its normal boiling point, is -
(A) 29.23 torr (B) 30.4 torr (C) 35.00 torr (D) 40.00 torr
- Q.12** The vapour pressure of a liquid decreases by 10 torr when a non-volatile solute is dissolved. The mole fraction of the solute in solution is 0.1. What would be the mole fraction of the liquid if the decrease in vapour pressure is 20 torr, the same solute being dissolved -
(A) 0.2 (B) 0.9 (C) 0.8 (D) 0.6
- Q.13** The mole fraction of the solvent in the solution of a non-volatile solute is 0.980. The relative lowering of vapour pressure is -
(A) 0.01 (B) 0.980 (C) 0.02 (D) 0.49
- Q.14** The vapour pressure of a solution of a non-volatile solute B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of the solute, what is the weight ratio of solvent to solute.
(A) 0.15 (B) 5.7 (C) 0.2 (D) none of these
- Q.15** The vapour pressure of water at room temperature is 23.8 mm Hg. The vapour pressure of an aqueous solution of sucrose with mole fraction 0.1 is equal to -
(A) 23.9 mm Hg (B) 24.2 mm Hg (C) 21.42 mm Hg (D) 31.44 mm Hg
- Q.16** The vapour pressure of pure A is 10 torr and at the same temperature when 1 g of B is dissolved in 20 g of A, its vapour pressure is reduced to 9.0 torr. If the molecular mass of A is 200 amu, then the molecular mass of B is -
(A) 100 amu (B) 90 amu (C) 75 amu (D) 120 amu
- Q.17** The vapour pressure of pure benzene C_6H_6 at 50°C is 260 Torr. How many moles of nonvolatile solute per mole of benzene are required to prepare a solution of benzene having a vapour pressure of 167.0 Torr at 50°C ?
(A) 0.305 mol (B) 0.605 mol (C) 0.336 mol (D) 0.663 mol
- Q.18** Lowering of vapour pressure due to a solute in 1 molal aqueous solution at 100°C is -
(A) 13.44 Torr (B) 14.12 Torr (C) 312 Torr (D) 352 Torr
- Q.19** How many grams of sucrose must be added to 360 g of water to lower the vapour pressure by 1.19 mmHg at a temperature at which pressure of pure water is 25 mm Hg ?
(A) 342 g (B) 360 g (C) 375 g (D) 380 g

(ii) Vapour Pressure of a Solution Containing Two Volatile Liquids

Raoult's law states that the partial vapour pressure of a component of a solution of two miscible liquids A and B at a given temperature is equal to the product of the vapour pressure of the pure component at that temperature and its mole fraction in the solution.

Mathematical Expression: Let us assume that a solution has n_A moles of liquid A and n_B moles of liquid B. Let P_A° be the vapour pressure of the pure liquid A and P_B° is the vapour pressure of the pure liquid B.

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

According to Raoult's law,

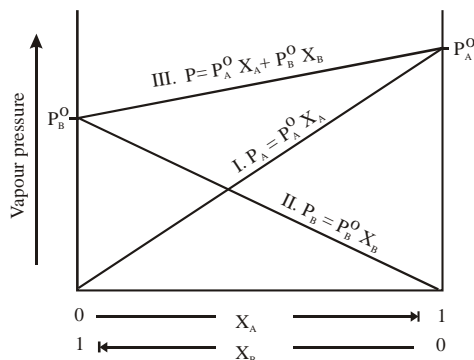
$$P_A = P_A^\circ X_A \quad (\text{where } P_A \text{ is the partial vapour pressure of liquid A in the solution})$$

Similarly, $P_B = P_B^\circ X_B$ (P_B - partial vapour pressure of B in the solution)

The total vapour pressure of an ideal solution containing components A and B is the sum of partial vapour pressures of all the components (Dalton's law of partial pressures)

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$$P = P_A + P_B = P_A^0 X_A + P_B^0 X_B \quad \text{.....(1)}$$



$$\square X_A + X_B = 1 \quad \Rightarrow \quad X_A = 1 - X_B$$

$$\therefore P = P_A^0 (1 - X_B) + P_B^0 X_B \quad \Rightarrow \quad P_A^0 - P_A^0 X_B + P_B^0 X_B$$

$$P = P_A^0 + (P_B^0 - P_A^0) X_B \quad \text{.....(2)}$$

About relation shows that graph between P and X_B is a straight line having slope $P_B^0 - P_A^0$ and intercept P_A^0

$$\text{Similarly } P = P_B^0 + (P_A^0 - P_B^0) X_A \quad \text{.....(3)}$$

Above figure shows the relationship between partial vapour pressure and mole fraction of an ideal solution at constant temperature.

1. Straight line I represents the plot of vapour pressure of liquid A (P_A) and its mole fraction (X_A). According to Raoult's law this should be a straight line when

$$X_A = 0 \quad P_A = 0, \quad X_A = 1, \quad P_A = P_A^0$$

When mole fraction of liquid A is $X_A = 1$, the liquid A is pure and its vapour pressure is equal to P_A^0 as shown by line (I)

2. Straight line II represents the plot of partial vapour pressure of liquid (B) P_B and its mole fraction (X_B). According to Raoult's law, this should be a straight line. when

$$X_B = 0 \quad P_B = 0, \quad X_B = 1, \quad P_B = P_B^0$$

When mole fraction of liquid B is $X_B = 1$, the liquid B is pure and its vapour pressure is equal to P_B^0 as shown by line (II).

3. Straight line (III) represents the total vapour pressure, P , of the solution for any composition and is given by the sum of the partial vapour pressure of liquids of A and B.

$$P = P_A + P_B$$

Illustration 7. An aqueous solution containing 28% by mass of a liquid A (mol. mass = 140) has a vapour pressure of 160 mm at 37°C. Find the vapour pressure of the pure liquid A. (The vapour pressure of water at 37°C is 150 mm.)

Solution : For two miscible liquids,

$$P_{\text{total}} = P_A + P_B = P_A^0 X_A + P_B^0 X_B \quad n_A = \frac{28}{140} = 0.2,$$

$$\text{Liquid B is water. Its mass is } (100 - 28), \text{ i.e. } 72. \quad n_B = \frac{72}{18} = 4.0$$

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Total number of moles = $0.2 + 4.0 = 4.2$

Given $P_{\text{total}} = 160 \text{ mm}$, $P_B^0 = 150 \text{ mm}$

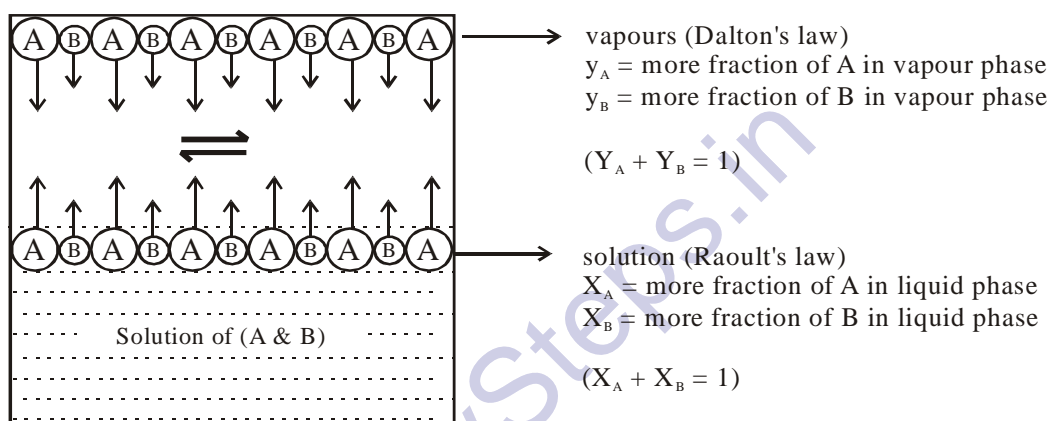
So
$$160 = \frac{0.2}{4.2} \times P_A^0 + \frac{4.0}{4.2} \times 5.0$$

$$P_A^0 = \frac{17.15 \times 4.2}{0.2} = 360.15 \text{ mm}$$

4. Determination of composition in vapour phase

Dalton's Law v/s Raoult's Law:

The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures. Let the mole fractions of vapours A and B be Y_A and Y_B respectively. Let p_A and p_B be the partial pressure of vapours A and B respectively and total pressure P .



From Raoult's law $P = P_A^0 X_A + P_B^0 X_B$
 $P_A = P_A^0 X_A$ and $P_B = P_B^0 X_B$

From Dalton's law,

Partial pressure = Mole fraction \times Total pressure

For A $P_A = y_A \times P$

$$P_A^0 X_A = y_A \times P \quad \Rightarrow \quad y_A = \frac{P_A^0 X_A}{P} \quad \dots(1)$$

Above formula is used for calculation of mole fraction of A in vapour phase

For B, $P_B = y_B \times P$

$$P_B^0 X_B = y_B \times P \quad \Rightarrow \quad y_B = \frac{P_B^0 X_B}{P} \quad \dots(2)$$

Above formula is used for calculation of mole fraction of B in vapour phase

From (1), $X_A = \frac{P \times y_A}{P_A^0}$

From (2) $X_B = \frac{P \times y_B}{P_B^0}$

on adding $X_A + X_B = \frac{P \times y_A}{P_A^0} + \frac{P \times y_B}{P_B^0} = 1$

$$\Rightarrow \frac{1}{P} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0} \quad \dots(3)$$

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Above formula is used to calculate total vapour pressure when mole fractions are given in vapour phase

Avoid confusion

$P = P_A^0 X_A + P_B^0 X_B \Rightarrow$ This formula is used to calculate total pressure when mole fraction are given in liquid phase

$\frac{1}{P} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0} \Rightarrow$ This formula is used to calculate total pressure when mole fraction are given in vapour phase

Note: Thus, in case of ideal solution the vapour phase is phase is richer with more volatile component i.e., the one having relatively greater vapour pressure.

Illustration: 8. The vapour pressures of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour.

Solution: No. of moles of $C_2H_5OH = \frac{60}{46} = 1.304$, No. of moles of $CH_3OH = \frac{40}{32} = 1.25$

$$'X_A' \text{ of ethyl alcohol} = \frac{1.304}{1.304 + 1.25} = 0.5107$$

$$'X_B' \text{ of methyl alcohol} = \frac{1.25}{1.304 + 1.25} = 0.4893$$

$$\text{Partial pressure of ethyl alcohol} = X_A \cdot P_A^0 = 0.5107 \times 44.5 = 22.73 \text{ mm Hg}$$

$$\text{Partial pressure of methyl alcohol} = X_B \cdot P_B^0 = 0.4893 \times 88.7 = 43.40 \text{ mm Hg}$$

$$\text{Total vapour pressure of solution} = 22.73 + 43.40 = 66.13 \text{ mm Hg}$$

$$\begin{aligned} \text{Mole fraction of methyl alcohol in the vapour} &= \frac{\text{Partial pressure of } CH_3OH}{\text{Total vapour pressure}} \\ &= \frac{43.40}{66.13} = 0.6563 \end{aligned}$$

2. Daily Practice Problem Sheet

- Q.1** An aqueous solution containing liquid A (M. wt. = 128) 64% by weight has a V. P. of 145 mm. If the vapour pressure of water is 155 mm then vapour pressure of A at the same temperature will be -
(A) 205 mm (B) 105 mm (C) 185 mm (D) 52.5 mm
- Q.2** The vapour pressure of pure ethylene bromide and propylene bromide are 170 and 127 mm of Hg at a temperature. Find out :
- The vapour pressure of ethylene bromide & propylene bromide in a 60% by weight solution of ethylene bromide in propylene bromide at same temperature, is -
(A) 52.4 mm, 24.31 mm (C) 52.4 mm, 48.63 mm
(C) 104.9 mm, 48.63 mm (D) 104.9 mm, 24.31 mm
 - Total vapour pressure of solution, is -
(A) 153.53 mm (B) 76.71 mm (C) 101.03 mm (D) 129.21 mm

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- Q.3** Two liquids A and B form ideal solution at 300 K. The vapour pressure of a solution containing one mole of A and four mole of B is 560 mm of Hg. At the same temperature if one mole of B is taken out from the solution, the vapour pressure of solution decreases by 10 mm of Hg. Vapour pressures of A and B in pure state will be-
(A) 330, 550 (B) 200, 300 (C) 400, 600 (D) 800, 1200
- Q.4** The vapour pressure of two volatile liquid mixture is $P_T = (5.3 - 2X_B)$ in cm of Hg ; where X_B is mole fraction of B in mixture. What are vapour pressure of pure liquids A and B ?
(A) 3.3 and 2.1 cm of Hg (B) 2.3 and 3.3 cm of Hg
(C) 5.3 and 2.3 cm of Hg (D) 5.3 and 3.3 cm of Hg
- Q.5** A mixture contains 1 mole volatile liquid A ($P_A^\circ = 100$ mm Hg) and 3 moles volatile liquid B ($P_B^\circ = 80$ mm). If solution be haves ideally, total vapour pressure of the solution is approximately -
(A) 80 mmHg (B) 85 mmHg (C) 90 mmHg (D) 92 mmHg
- Q.6** At 40°C the vapour pressure in torr of methanol and ethanol solution is $P = 119x + 135$ where x is the mole fraction of methanol, hence,
(A) vapour pressure of pure methanol is 119 torr
(B) vapour pressure of pure ethanol is 135 torr
(C) vapour pressure of equimolar mixture of each is 127 torr
(D) mixture is completely immiscible
- Q.7** Vapour pressure of pure A is 70 mm of Hg at 25°C it forms an ideal solution with B in which mole fraction of A is 0.8. If vapour pressure of solution is 84 mm of Hg at 25°C, the vapour pressure of pure B at 25°C is -
(A) 1 atm (B) 14 mm of Hg (C) 140 mm of Hg (D) 56 cm of Hg
- Q.8** Vapour pressure (in torr) of an ideal solution of two liquids A and B is given by : $P = 52 X_A + 114$ where X_A is the mole fraction of A in the mixture. The vapour pressure (in torr) of equimolar mixture of the two liquids will be -
(A) 166 (B) 83 (C) 140 (D) 280
- Q.9** Solution of two volatile liquids A and B obey Raoult's law. At a certain temperature, it is found that when the total vapour pressure above solution is 400 mm of Hg, the mole fraction of A in vapour phase is 0.45 and in liquid phase 0.65 then the vapour pressures of two pure liquids at the same temperature will be -
(A) 138.4 mm, 628.57 mm (B) 276.9 mm, 628.57 mm
(C) 276.9 mm, 314.28 mm (D) 138.4 mm, 314.28 mm
- Q.10** The vapour pressure of benzene and toluene at 20°C are 75 mm of Hg and 22 mm of Hg respectively. 23.4 g of benzene and 64.4g of toluene are mixed. If two forms ideal solution, the mole fraction of benzene in vapour phase when vapours are in equilibrium with liquid mixture, is -
(A) 0.59, 0.41 (B) 0.25, 0.75 (C) 0.5, 0.5 (D) 0.35, 0.65
- Q.11** The vapour pressure of two liquids are 15000 and 30000 in a unit. When equimolar solution of liquids is made. Then the mole fraction of A and B in vapour phase will be -
(A) $\frac{2}{3}, \frac{1}{3}$ (B) $\frac{1}{3}, \frac{2}{3}$ (C) $\frac{1}{2}, \frac{1}{2}$ (D) $\frac{1}{4}, \frac{3}{4}$
- Q.12** At 30°C, the vapour pressure of pure ether is 646 mm and of pure acetone is 283 mm. Find out the mole fraction of each component in vapour state for the solution of two having mole fraction of ether 0.50. Assume ideal behaviour.
(A) 0.20, 0.80 (B) 0.799, 0.201 (C) 0.695, 0.305 (D) 0.535, 0.465

LIQUID SOLUTIONS

- Q.13** Benzene and toluene form an ideal solution. The vapour pressure of benzene and toluene are respectively 75 mm and 22 mm at 20°C. If the mole fraction of benzene and toluene in vapour phase are 0.63 and 0.37 respectively, then :
- The vapour pressure of mixture is -
 (A) 39.68 mm (B) 79.32 mm (C) 58.56 mm (D) 29.24 mm
 - Mole fraction of benzene & toluene in liquid phase is -
 (A) 0.2, 0.8 (B) 0.63, 0.37 (C) 0.54, 0.46 (D) 0.33, 0.67
- Q.14** At 90°C, the vapour pressure of toluene is 400 mm and that of xylene is 150 mm. The composition of liquid mixture that will boil at 90°C when the pressure of mixture is 0.5 atm, is -
 (A) 0.8, 0.2 (B) 0.75, 0.25 (C) 0.92, 0.08 (D) 0.66, 0.34
- Q.15** V. P. of pure A $p_A^\circ = 100$ mmHg
 V. P. of pure B $p_B^\circ = 150$ mmHg
 Distillate of vapours of a solution containing 2 moles A and 3 moles B will have total vapour pressure, approximately, on condensation
 (A) 135 mm (B) 130 mm (C) 140 mm (D) 145 mm
- Q.16** 1 mole benzene ($P^\circ = 42$ mm) and 2 moles toluene ($P^\circ = 36$ mm) will have
 (A) total vapour pressure 38 mm
 (B) mole fraction of vapours of benzene above liquid mixture is 7/19
 (C) ideal behaviour (D) all of the above
- Q.17** At a given temperature, the vapour pressure of pure A and B is 108 and 36 torr respectively. What will be the mole fraction of B in the vapour phase which is in equilibrium with a solution containing equimole fraction of A and B, under ideal behaviour conditions ?
 (A) 0.25 (B) 0.33 (C) 0.50 (D) 0.60
- Q.18** A solution of benzene ($p^\circ = 120$ torr) and toluene ($p^\circ = 80$ torr) has 2.0 mol of each component. At equilibrium the mol fraction of toluene in vapour phase is -
 (A) 0.50 (B) 0.25 (C) 0.60 (D) 0.40
- Q.19** Liquids A and B form an ideal solution and the former has stronger intermolecular forces. If X_A and X'_A are the mole fractions of A in the solution and vapour in equilibrium, then -
 (A) $\frac{X'_A}{X_A} = 1$ (B) $\frac{X'_A}{X_A} > 1$ (C) $\frac{X'_A}{X_A} < 1$ (D) $X'_A + X_A = 1$
- Q.20** Mole fraction of a liquid A in an ideal mixture with another liquid b is X_A . If X'_A is the mole fraction of component A in the vapour in equilibrium, the total pressure of the liquid mixture is -
 (P_A° = vapour pressure of pure A ; P_B° = vapour pressure of pure B)
 (A) $P_A^\circ \frac{X'_A}{X_A}$ (B) $\frac{P_A^\circ X_A}{X'_A}$ (C) $\frac{P_B^\circ X'_A}{X_A}$ (D) $\frac{P_B^\circ X_A}{X'_A}$
- Q.21** Two liquids A and B have $P_A^\circ : P_B^\circ = 1 : 3$ at a certain temperature. If the mole fraction ratio of $x_A : x_B = 1 : 3$, the mole fraction of A in vapour in equilibrium with the solution at a given temperature is -
 (A) 0.1 (B) 0.2 (C) 0.5 (D) 1.0
- Q.22** At a certain temperature pure liquid A and liquid B have vapour pressures 10 torr and 37 torr respectively. For a certain ideal solution of A and B, the vapour in equilibrium with the liquid has the components A and B in the partial pressure ratio $P_A : P_B = 1 : 7$. What is the mole fraction of A in the solution ?
 (A) 0.346 (B) 0.654 (C) 0.5 (D) none of these
- Q.23** Mole fraction of the toluene in the vapour phase which is in equilibrium with a solution of benzene ($p^\circ = 120$) and toluene ($p^\circ = 80$) having 2.0 moles of each, is -
 (A) 0.50 (B) 0.25 (C) 0.60 (D) 0.40

LIQUID SOLUTIONS

- Q.24** The vapour pressure of pure liquid A at 300 K is 575 torr and that of pure liquid B is 390 torr. These two compounds form ideal liquid and gaseous mixtures. The mole fraction of A in the vapour phase is 0.35. Then :
- The total pressure of the mixture is
(A) 526 torr (B) 965 torr (C) 440 torr (D) 715 torr
 - composition of the liquid mixture is -
(A) A = 27%, B = 73% (B) A = 57 %, B = 43 %
(C) A = 33% . B = 67% (D) A = 30%, B = 70%
- Q.25** 64 gm of methanol & 46 gm of ethanol forms in an ideal solution at 350 K. If the vapour pressure of methanol and ethanol at 350 K are 8.1×10^4 and $4.5 \times 10^4 \text{ N m}^{-2}$ respectively, then mole fraction of methanol in vapour phase is -
(A) 0.62 (B) 0.22 (C) 0.80 (D) 0.78
- Q.26** Two liquids A and B forms an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75. The vapour pressure of pure A and B respectively are -
(A) 165.54 torr , 772.00 torr (B) 240.24 torr , 840.00 torr
(C) 213.33 torr, 960.00 torr (D) 312.15 torr , 865.00 torr
- Q.27** Vapour pressure of a mixture of benzene and toluene is given by $P = 179 x_B + 92$ where x_B is mole fraction of benzene. Determine :
- vapour pressure of the solution obtained by mixing 936 gm of benzene and 736 gm of toluene
(A) 199.4 mm (B) 271 mm (C) 280 mm (D) 289 mm
 - If vapours are removed and condensed into liquid then what will be the ratio of mole fraction of benzene and toluene in first condensate -
(A) 2.8 (B) 1.5 (C) 3.5 (D) 4.5
 - This condensed liquid again brought to the same temperature then what will be the mole fraction of benzene in vapour phase -
(A) 0.07 (B) 0.93 (C) 0.65 (D) 0.45
- Q.28** Benzene and toluene form nearly ideal solutions. If at 27°C the vapour pressures of pure toluene and pure benzene are 32.06 mm and 103.01 mm respectively, the vapour pressure of a solution containing 0.60 mole fraction of toluene, is -
(A) 60.44 mm (B) 30.22 mm (C) 120.12 mm (D) 76.52 mm
- Q.29** An aqueous solution containing 28% by mass of a liquid A (mol. mass = 140) has a vapour pressure of 160 mm at 37°C. The vapour pressure of water at 37°C is 150 mm, then the pressure of pure liquid A, is -
(A) 180.22 mm (B) 300.32 mm (C) 360.15 mm (D) 276.55 mm
- Q.30** The vapour pressure of ethyl alcohol and methyl alcohol are 45 mm and 90 mm. An ideal solution is formed at the same temperature by mixing 60 g of $\text{C}_2\text{H}_5\text{OH}$ with 40 g of CH_3OH . Total vapour pressure of the solution is approximately -
(A) 70 mm (B) 35 mm (C) 105 mm (D) 140 mm

5. Type of solutions

(i) Ideal Solution

An ideal solution may be defined as the one which obeys Raoult's law over all concentration ranges at a given temperature. The total vapour pressure of an ideal solution containing liquids A and B is given by the following equation.

$$P = P_A + P_B = P_A^\circ X_A + P_B^\circ X_B$$

LIQUID SOLUTIONS

In an ideal solution of two components A and B, all attractive forces between A and B molecules or between A and A molecules or between B and B molecules (A–B, A–A and B–B) must be identical so that the escaping tendency of an A or B molecule is independent of whether it is surrounded by A molecules, B, molecules or varying proportions of A and B molecules. The escaping tendency of pure liquid A in solution remains the same. Similarly the escaping tendency of B remains the same. Liquids form ideal solution only when they have nearly same molecular size and related constitution so that they have similar molecular environment in the pure state as well as in solution. A perfect ideal solution is rare but many liquids form nearly ideal solution. Liquid heptane and hexane form an ideal solution because the interaction between a hexane molecule and another hexane molecule is the same as the interaction between two heptane molecules other examples of **ideal solutions** are:

benzene + toluene,	chlorobenzene + bromobenzene;
ethyl bromide + ethyl iodide;	n-butyl chloride + n-butyl bromide
ethyl alcohol + methyl alcohol	

Conditions for Forming Ideal Solution: Two liquids on mixing form an ideal solution only when

1. both have similar structures and polarity so that they have similar molecular environment.
2. both have similar molecular sizes.
3. both have identical intermolecular forces.

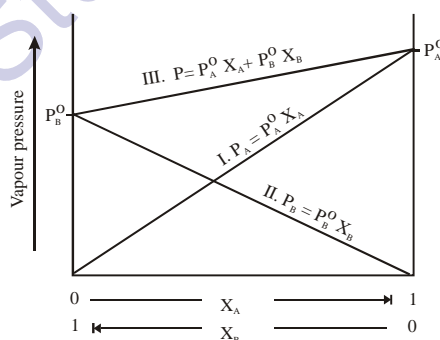
Characteristics Of Ideal Solution:

Mixing of two substances results in an ideal solution only when:

1. They obey Raoult's Law
2. $\Delta H_{\text{mixing}} = 0 \Rightarrow$ that is no heat is absorbed or released during dissolution
3. $\Delta V_{\text{mixing}} = 0 \Rightarrow$ that is the total volume of the solution is equal to the sum of the volume of the pure liquids mixed to form the solution.

Graphical Representation of Vapour Pressure of Ideal Solutions:

Figure shows the relationship between partial vapour pressure and mole fraction of an ideal solution at constant temperature.



Note : Components of ideal solution can be separated in pure form by fractional distillation

(ii) Non-Ideal Solutions

Solutions which do not obey Raoult's law over all concentration ranges at constant temperature are called non-ideal solutions.

Characteristic of nonideal solution

- (i) $P_A \neq P_A^0 X_A + P_B \neq P_B^0 X_B, P \neq P_A^0 X_A + P_B^0 X_B$
- (ii) $\Delta V_{\text{mix}} \neq 0,$
- (iii) $\Delta H_{\text{mix}} \neq 0$

LIQUID SOLUTIONS

Types of Non-Ideal Solutions

1. Non ideal solutions showing +ve deviation
2. Non ideal solutions showing –ve deviation.

1. Non ideal solutions showing +ve deviation

Condition for forming non-ideal solution showing +ve deviation from Raoult's law.

Two liquids A and B on mixing form this type of solution when

1. A—B attractive force should be weaker than A—A and B—B attractive forces.
2. 'A' and 'B' have different shape, size and character.
3. 'A' and 'B' escape easily showing higher vapour pressure than the expected value.

Characteristic of non-ideal solution showing +ve deviation

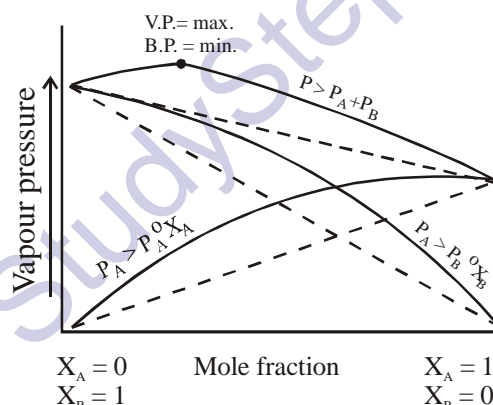
1. Do not obey Raoult's law
2. $\Delta H_{\text{mix}} > 0$. (endothermic dissolution heat is absorbed.)
3. $\Delta V_{\text{mix}} > 0$. (Volume is increased after dissolution)
4. $p_A > p_A^0 X_A$; $p_B > p_B^0 X_B$, $\therefore p_A + p_B > p_A^0 X_A + p_B^0 X_B$

Example :

acetone + ethanol	acetone + CS ₂	water + methanol;
water + ethanol;	CCl ₄ + toluene;	CCl ₄ + CHCl ₃ ;
etone + benzene;	CCl ₄ + CH ₃ OH;	cyclohexane + ethanol

a c -

Graphical representation of vapour of non-ideal solution showing +ve deviation



2. Non ideal solutions showing –ve deviation.

Condition for forming non-ideal solution showing +ve deviation from Raoult's law.

Two liquids A and B on mixing form this type of solution when

1. A—B attractive force should be greater than A—A and B—B attractive forces.
2. 'A' and 'B' have different shape, size and character
3. Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.

Characteristic of non-ideal solution showing +ve deviation

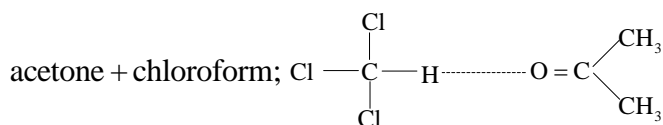
1. Do not obey Raoult's law.
2. $\Delta H_{\text{mix}} < 0$. (Exothermic dissolution; heat is evolved.)
3. $\Delta V_{\text{mix}} < 0$. (Volume is decreased during dissolution)
4. $p_A < p_A^0 X_A$; $p_B < p_B^0 X_B$, $\therefore p_A + p_B < p_A^0 X_A + p_B^0 X_B$

LIQUID SOLUTIONS

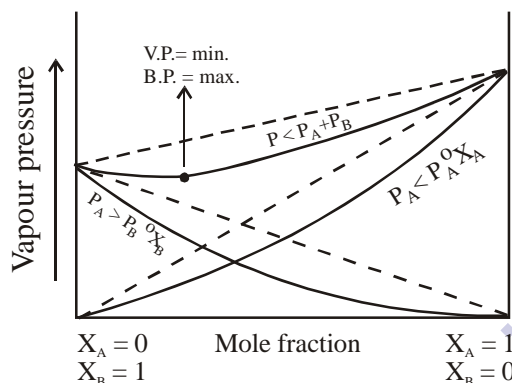
Example

acetone + aniline;
chloroform + diethyl ether,
chloroform + benzene
water + HCl

$\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$;
acetic acid + pyridine;
 $\text{H}_2\text{O} + \text{HNO}_3$;



Graphical representation of vapour of non-ideal solution showing +ve deviation



(iii) Azeotropes

The non-ideal solution showing large deviations from Raoult's law can not be purified by distillation. A solution at certain composition which continues to boil at constant temperature without change in the composition of the solution and its vapour is called an AZEOTROPE or constant boiling mixture. Azeotropes are of two types:

1. **Azeotropes with Max. vapour pressure and Min. BP :** When liquid in a solution do not have great chemical affinity for each other (+ve deviation from ideality) their higher escape tendencies increase the vapour pressure much more than expected on the basis of Raoult's law. In many cases, the deviations are so extreme as to lead to a maximum in the curve. The point of maximum vapour pressure means that the bp at this composition will be minimum and constant.

Example of Minimum Boiling Azeotrope

Components			Boiling point (K)		
A	B	Mass% of B	A	B	Azeotrope
H_2O	$\text{C}_2\text{H}_5\text{OH}$	95.57	373	351.3	351.10
H_2O	$\text{C}_3\text{H}_7\text{OH}$	71.69	373	370.0	350.72
CHCl_3	$\text{C}_2\text{H}_5\text{OH}$	67.00	334	351.3	332.30

2. **Azeotropes with Min. vapour pressure and Max. bp :** When liquids in solution form chemical bonds (–ve deviation from ideality), their escape tendencies and hence the vapour pressure decreases than expected on the basis of Raoult's law. In many cases, the maximum in the temperature composition curve is obtained. The point of minimum vapour pressure in the curve means that the bp of this composition will be max. and constant.

LIQUID SOLUTIONS

Examples of Max. Boiling Azeotrope

Components			Boiling point (K)		
A	B	Mass% of B	A	B	Azeotrope
H ₂ O	HCl	20.3	373	188	383
H ₂ O	HNO ₃	58.0	373	359	393.5
H ₂ O	HClO ₄	71.6	373	383	476

6. Colligative Properties

The property of a solution which depends upon the fraction of solute particles and solvent particles and not upon the chemical nature of solute is called a colligative property. Greater the no. of particles of solute in solution, greater is the extent to which colligative property is affected.

Type of colligative properties

- | | |
|------------------------------------|---------------------------------|
| (i) Lowering of vapour pressure | (ii) Elevation of Boiling point |
| (iii) Depression of Freezing point | (iv) Osmotic Pressure |

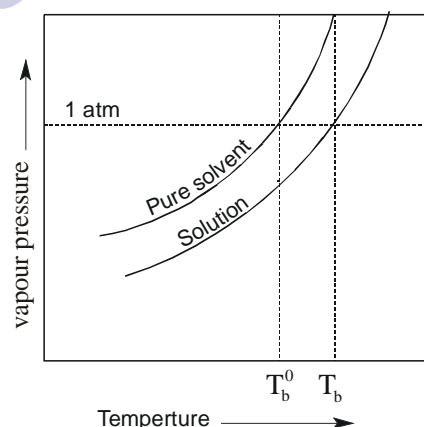
Factors that Affect the Colligative Property: The no. of solute particles in solution. To be more accurate, the colligative property depends upon the fraction of solute and solvent particles in solution.

- (1) Nature of the solvent
- (2) Independent of the nature of the solute
- (3) Extent of association and dissociation of solute particles in solution.

(i) Lowering of Vapour Pressure: Vapour pressure lowering of a solution has already been explained under Raoult's Law. It was derived that the relative lowering of vapour pressure is given by the equation

$$\frac{P_A^0 - P_A}{P_A^0} = X_B = \frac{n_B}{n_A + n_B}$$

(ii) Elevation of Boiling Point: The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. When the atmospheric pressure is 1 atm, boiling point is called the normal boiling point.



Plot of variation of vapour pressure elevation of boiling point

The vapour pressure of a liquid decreases when a non-volatile solute is dissolved in it. The decreased vapour-pressure means that the solution would have to be heated to a higher temperature so that its vapour pressure becomes equal to the atmospheric pressure. In other words, the boiling point of the solution T_b is higher than the boiling point of the pure solvent T_b^0 . The difference $T_b - T_b^0$ is called the boiling point elevation and denoted by ΔT_b .

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$$UT_b = T_b - T_b^0 \quad \text{.....(1)}$$

It is found that the elevation of boiling point is directly proportional to the number of moles of the solute in a given amount of the solvent (m).

$$\Delta T \propto m \quad \Rightarrow \quad UT_b = K_b \cdot m \quad \text{.....(2)}$$

where m is the molality of the solution and K_b is a constant for a given solvent known as boiling-point elevation constant or molal boiling point elevation constant or ebullioscopic constant of solution.

Molal Elevation Constant or Ebullioscopic Constant: When molality of the solution is 1m, (1 mole of the solute is dissolved in 1 kg of the solvent) the above equation reduces to

$$\Delta T_b = K_b \times 1m = K_b$$

This indicates that molal elevation constant of a liquid (K_b) is equal to elevation of boiling point when molality of the solution is 1 m. the unit of K_b is K m^{-1} . $\text{K (mol/kg)}^{-1} = \text{K kg mol}^{-1}$.

Determination of K_b of solvent :

$$K_b = \frac{RT_b^2}{1000L_v} \quad \text{.....(3)}$$

where R is molar gas constant, T_b is the boiling point of the solvent on Kelvin scale and L_v the latent heat of vaporization of solvent in calories per gram.

For water
$$K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515 \text{ K-kg/mol}$$

Illustration 9. Estimate the boiling point of a solution of 25.0g of urea NH_2CONH_2 plus 25.0g of thiourea NH_2CSNH_2 in 500g of chloroform, CHCl_3 . The boiling point of pure chloroform is 61.2°C , K_b of chloroform = 3.63 K m^{-1} .

Solution: Moles of urea = $\frac{\text{Mass of urea}}{\text{Molecular mass of urea}} = \frac{25.0\text{g}}{60\text{g/mol}} = 0.42\text{mol}$

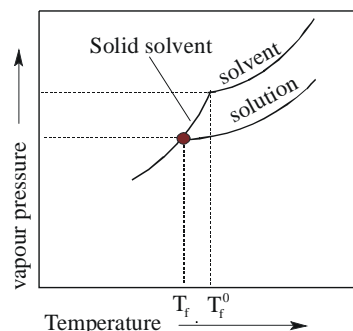
Moles of thiourea = $\frac{25.0}{76 \text{ g/mol}} = 0.33\text{mol}$ \therefore Total moles of solute = $0.42 + 0.33 = 0.75$

Molality, $m = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \frac{0.75\text{mol}}{(500\text{g}/1000\text{g})\text{kg}} = 1.50\text{m}$

$$\Delta T_b = T_b - T_b^0 = K_b \cdot m = 3.63 \times 1.50 = 5.44\text{K} = 5.445^\circ\text{C}$$

$$T_b = 5.445^\circ\text{C} + T_b^0 = 5.445^\circ\text{C} + 61.2^\circ\text{C} = 66.645^\circ\text{C}$$

(iii) Depression in Freezing Point: The freezing point of a liquid is the temperature at which it begins to freeze and the crystallized solid and liquid are in equilibrium. At freezing point, the vapour pressure of the solid is equal to the vapour pressure of the liquid. When a dilute solution is cooled to freezing point, it is assumed that crystals of pure solvent always separate out first.



Plot of variation of vapour pressure of a solution with temperature and depression in freezing point.

LIQUID SOLUTIONS

The vapour pressure of a liquid decreases when a non-volatile solute is dissolved in it. Therefore, a solid-liquid equilibrium exists only at a temperature lower than the freezing point of the pure solvent. In other words, for a solid to have the same vapour pressure as that of the solution, the freezing point should lower down. If T_f^0 is the freezing point of the pure solvent and T_f that of the solution, the difference $T_f^0 - T_f$ is called the freezing point depression and denoted by ΔT_s

$$\Delta T_s = T_f^0 - T_f \quad \text{.....(1)}$$

It is found that the depression in freezing point is directly proportional to the number of moles of the solute in a solute given amount of the solvent.

$$\Delta T_f = K_f \cdot m \quad \text{.....(2)}$$

where m is the molality of the solution and K_f is a constant for a given solvent known as molal depression constant or cryoscopic constant.

Molal Depression Constant or Cryoscopic Constant: When molality of the solution is 1m, (1 mole of the solute is dissolved in 1 kg of the solvent) the above equation reduces to

$$\Delta T_f = K_f \times 1m = K_f$$

This indicates that molal depression constant of a liquid (K_f) is equal to depression of freezing point when molality of the solution is 1 m. the unit of K_f is K m^{-1} . $\text{K (mol/kg)}^{-1} = \text{K kg mol}^{-1}$.

Determination of K_f of solvent

K_f is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_f = \frac{RT_f^2}{1000L_f} \quad \text{.....(3)}$$

where T_f is the freezing point of solvent in absolute scale and L_f the latent heat of fusion in calories per gram of the solvent. For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86 \text{ K-kg/mole}$$

Illustration 10. What is the percent by mass of iodine needed to reduce the freezing point of benzene to 3.5°C ? The freezing point and cryoscopic constant of pure benzene are 5.5°C and 5.12 K/m respectively.

Solution: $\Delta T_f = T_f^0 - T_f = K_f \cdot m$
 $5.5^\circ\text{C} - 3.5^\circ\text{C} = 5.12 \times m$

$$m = \frac{2}{5.12} = 0.39 \text{ molal}$$

$$\therefore \text{Mass of iodine needed for 1000g of benzene} = m \times \text{molecular mass of iodine } I_2$$

$$= 0.39 \text{ mol/kg} \times 254 \text{ g/mol} = 99.06 \text{ g/kg}$$

$$\therefore 1000\text{g} + 99.06\text{g solution contains } 99.06\text{g } I_2$$

$$100\text{g solution contains } \frac{99.06\text{g} \times 100}{1099.06\text{g}} = 9.01\%$$

3. Daily Practice Problem Sheet

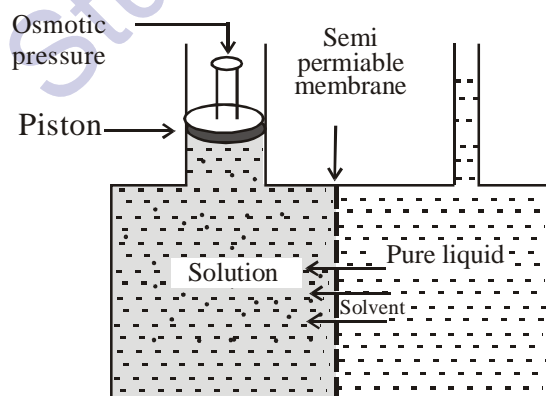
- Q.1** A solution containing 0.52 g of $C_{10}H_8$ in CCl_4 produced an elevation in boiling point by $0.402^\circ C$. On the other hand a solution of 0.62 g of an unknown solute dissolved in same amount of CCl_4 produced an elevation by $0.65^\circ C$. Molecular weight of solute is -
(A) 85.53 (B) 181.51 (C) 94.38 (D) 160.62
- Q.2** 0.65 g naphthalene ($C_{10}H_8$) was dissolved in 100 g methyl acetate. Elevation of b. pt of methyl acetate solution was $0.103^\circ C$. If b. pt. of pure methyl acetate is $57^\circ C$, its molar heat of vaporisation will be -
(A) $8.96 \text{ kcal mol}^{-1}$ (B) $7.946 \text{ kcal mol}^{-1}$ (C) $6.24 \text{ kcal mol}^{-1}$ (D) $15.65 \text{ kcal mol}^{-1}$
- Q.3** When 174.5 mg of octa atomic sulphur is added to 78 g of bromine, the boiling point of bromine is -
[Given K_b for Br_2 is $5.2 \text{ K mol}^{-1} \text{ kg}$ and b. pt. of Br_2 is 332.15 K]
(A) 415.23 K (B) 330 K (C) 220.92 K (D) 332.19 K
- Q.4** 4.00 g of substance A, dissolved in 100 g H_2O depressed the f. pt. of water by $0.1^\circ C$. While 4 g of another substance B, depressed the f. pt. by $0.2^\circ C$. What is the relation between molecular weights of the two substance -
(A) $M_A = 4M_B$ (B) $M_A = M_B$ (C) $M_A = 0.5M_B$ (D) $M_A = 2M_B$
- Q.5** An aqueous solution containing 5% by weight of urea and 10% by weight of glucose. Freezing point of solution is [K_f for H_2O is $1.86 \text{ K mol}^{-1} \text{ kg}$]
(A) $3.04^\circ C$ (B) $-3.04^\circ C$ (C) $-5.96^\circ C$ (D) $5.96^\circ C$
- Q.6** The amount of ice that will separate out from a solution containing 25 g of ethylene glycol in 100 g of water and is cooled to $-10^\circ C$, will be - [Given : K_f for $H_2O = 1.86 \text{ K mol}^{-1} \text{ kg}$]
(A) 50.0 g (B) 25.0 g (C) 12.5 gm (D) 30.0 gm
- Q.7** It has been found that minimum temperature recorded in a hill station is $-10^\circ C$. The amount of glycerine to be added to 40 dm^3 water used in car radiator, so that it does not freeze, is - [$\Delta H_{\text{fusion}} = 6.01 \text{ kJ mol}^{-1}$]
(A) 39.78 kg (B) 22.45 kg (C) 19.89 kg (D) 42.66 kg
- Q.8** In winter, the normal temperature in Kullu valley was found to be $-11^\circ C$. Is a 28% (by mass) aqueous solution of ethylene glycol suitable for a car radiator ? K_f for water = $1.86 \text{ K kg mol}^{-1}$.
(A) Yes (B) No (C) can't predict
- Q.9** The temperature at which ice will begin to separate from a mixture of 20 mass percent of glycol ($C_2H_6O_2$) in water, is - [$K_f(\text{water}) = 1.86 \text{ K kg mol}^{-1}$]
(A) 280.5 K (B) 265.5 K (C) 276.5 K (D) 269.5 K
- Q.10** The amount of urea to be dissolved in 500 ml of water ($K_f = 18.6 \text{ K mol}^{-1} 100 \text{ g solvent}$) to produce a depression of $0.186^\circ C$ in freezing point is -
(A) 0.3 gm (B) 3 gm (C) 6 gm (D) 9 gm
- Q.11** The molal boiling point constant of water is $0.53^\circ C$. When 2 mole of glucose are dissolved in 4000 gm of water, the solution will boil at -
(A) $100.53^\circ C$ (B) $101.06^\circ C$ (C) $100.265^\circ C$ (D) $99.47^\circ C$
- Q.12** The boiling point of an aqueous solution of a non-volatile solute is $100.15^\circ C$. What is the freezing point of an aqueous solution obtained by diluting the above solution with an equal volume of water ?
[K_b and K_f for water are 0.512 and $1.86 \text{ K molality}^{-1}$]
(A) $-0.544^\circ C$ (B) $-0.512^\circ C$ (C) $-0.272^\circ C$ (D) $-1.86^\circ C$
- Q.13** The freezing point of a solution prepared from 1.25 gm of non-electrolyte and 20 gm of water is 271.9 K . If molar depression constant is $1.86 \text{ K molality}^{-1}$. Then molar mass of the solute will be -
(A) 105.68 (B) 106.7 (C) 115.3 (D) 93.9

LIQUID SOLUTIONS

- Q.14** Elevation in b. p of a solution of non-electrolyte in CCl_4 is 0.60 . What is depression in f. p. for the same solution ? $K_f(\text{CCl}_4) = 30.00 \text{ kg mol}^{-1} \text{ K}$; $K_b(\text{CCl}_4) = 5.02 \text{ kg mol}^{-1} \text{ K}$.
 (A) 0° (B) 5.39° (C) 3.59° (D) 2.49°
- Q.15** A solution of a non-volatile solute in water has a boiling point of 375.3 K . The vapour pressure of water above this solution at 338 K is -
 [Given $p_0(\text{water}) = 0.2467 \text{ atm}$ at 338 K and K_b for water $= 0.52 \text{ K kg mol}^{-1}$]
 (A) 0.18 atm (B) 0.23 atm (C) 0.34 atm (D) 0.42 atm
- Q.16** Elevation in boiling point of an aqueous urea solution is 0.52° . ($K_b = 0.52 \text{ K kg mol}^{-1}$). Hence mole fraction of urea in this solution is -
 (A) 0.982 (B) 0.0567 (C) 0.943 (D) 0.018
- Q.17** Density of 1 M solution of a non-electrolyte $\text{C}_6\text{H}_{12}\text{O}_6$ is 1.18 g/mL . If $K_f(\text{H}_2\text{O})$ is $1.86 \text{ K kg mol}^{-1}$, solution freezes at -
 (A) 1.58°C (B) -1.86°C (C) -3.16°C (D) 1.86°C
- Q.18** When a solution containing $w \text{ g}$ of urea in 1 kg of water is cooled to -0.372°C , 200 g of ice is separated. If K_f for water is $1.86 \text{ K kg mol}^{-1}$, w is -
 (A) 4.8 g (B) 12.0 g (C) 9.6 g (D) 6.0 g
- Q.19** 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 $1 \text{ molal aq. urea solution}$ boils at 100.54°C at 1 atm. pressure)
 (A) 0.018° (B) 0.18° (C) 0.54° (D) 0.03°
- Q.20** Glucose is added to 1 litre water to such an extent that $\Delta T_f/K_f$ becomes equal to $1/1000$, the weight of glucose added is
 (A) 180 gm (B) 18 gm (C) 1.8 gm (D) 0.18 gm

(iv) Osmosis:

Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to a concentrated solution) is termed as osmosis.



Osmotic Pressure (π): The hydrostatic pressure built up on the solution which just stops osmosis. Alternatively, it may be defined as the pressure which must be applied to the concentrated solution in order to stop osmosis.

For dilute solutions $\pi = CRT = h\rho g$ (hydrostatic pressure)

Where C is the total molar concentration of all the free species present in the solution, h is the height developed by the column of the concentrated solution and ρ is the density of the solution in the column.

On the basis of osmotic pressure, the solutions can be classified in three classes.

LIQUID SOLUTIONS

- (a) Hypertonic solution:** When two solutions are being compared, then the solution with higher osmotic pressure is termed as hypertonic.
- (b) Hypotonic solution:** When two solutions are being compared, then the solution with lower osmotic pressure is termed as hypertonic.
- (c) Isotonic solutions:** Two solutions having same osmotic pressures at same temperature. (This implies $C_1 = C_2$).

Note: -Osmotic pressures can be determined quite accurately, hence it is used in the determination molecular weights of large proteins and similar substances.

Reverse Osmosis: If a pressure greater than the osmotic pressure is applied on the concentrated solution, the solvent starts to flow from concentrated solution to dilute solution (or pure solvent). This is reverse osmosis. One of its chief uses is desalination of sea water to get pure drinking water.

Illustration 11. Calculate osmotic pressure of 5% solution of cane sugar (sucrose) at 15°C.

Solution: m = mol. mass of sucrose ($C_{12}H_{22}O_{11}$) = 342

$$w = 5g \quad V = 100 \text{ mL} = 0.1 \text{ litre}$$

$$S = 0.082, \quad T = (15 + 273) = 288 \text{ K}$$

Applying the equation $PV = \frac{w}{m} ST$,

$$P = \frac{5}{342} \times \frac{1}{0.1} = 0.082 \times 288 = 3.453]$$

Illustration 12. Consider a vertical tube of cross-sectional area of 1cm^2 . The bottom of the tube is closed with a semipermeable membrane and 1 g glucose is placed in the tube. The closed end of the tube is immersed in pure water. What will be the height of the liquid level in the tube at equilibrium? The density of solution may be taken as 1g/cm^3 . What is the osmotic pressure at equilibrium at 25°C? Assume negligible depth of immersion of tube.

Solution: Let height in tube = h cm

$$V = (h \times 1) \text{ cm}^3 \quad \square \text{ Cross-sectional area} = 1\text{cm}^2$$

$$\pi V = nRT$$

$$\pi \times \left(\frac{h \times 1}{1000} \right) = \frac{1}{180} \times 0.0821 \times 298$$

$$\pi = \frac{134.92}{h} \text{ atm}$$

$$\pi = h \times d \times g$$

$$\frac{134.92}{h} = \frac{h \times 1}{100} \times \frac{9.8}{101.325} \quad 1 \text{ atm} = 101.325 \text{ KP}_a$$

$$h = 375 \text{ cm} = 3.75 \text{ m}$$

$$\pi = h \times d \times g = 3.75 \times 1 \times 9.8 = 36.7 \text{ KP}_a$$

[Ans. 3.75 m; 36.7 KP_a]

Illustration 13. A 5% solution of cane sugar is isotonic with 0.877% solution of urea. Calculate the molecular mass of urea if molecular mass of cane sugar is 342.

Solution: Let the molecular mass of urea be m_2

$$\text{Molarity of sugar} = \frac{w_1}{m_1 \times V_1} = \frac{5}{342 \times 0.1}$$

LIQUID SOLUTIONS

$$\text{Molarity of urea} = \frac{w_2}{m_2 \times V_2} = \frac{0.877}{m_2 \times 0.1}$$

For isotonic solutions,

$$\frac{w_1}{m_1 \times V_1} = \frac{w_2}{m_2 \times V_2} \Rightarrow \frac{5}{342 \times 0.1} = \frac{0.877}{m_2 \times 0.1}$$

$$m_2 = \frac{0.877 \times 342}{5} = 59.987$$

4. Daily Practice Problem Sheet

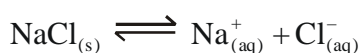
- Q.1** A solution containing 4 gm of a non-volatile organic solute per 100 ml was found to have an osmotic pressure equal to 500 cm of mercury at 27°C. The molecular weight of solute is -
(A) 14.97 (B) 29.44 (C) 149.7 (D) 137.2
- Q.2** The osmotic pressure of decimolar solution of glucose at 30°C is -
(A) 24.88 atm (B) 2.48 atm (C) 12.44 atm (D) 124.4 atm
- Q.3** A solution containing 8.6 gm urea in one litre was found to be isotonic with a 5% (wt/vol) solution of an organic volatile solute. The molecular weight of solute is -
(A) 348.9 (B) 34.89 (C) 861.2 (D) 86.12
- Q.4** The osmotic pressure of a solution containing 100 ml of 3.4% solution (w/v) of urea (m. wt. 60) and 50 ml of 1.6% solution (w/v) of cane-sugar (m. wt 342) at 27°C is -
(A) 10.56 atm (B) 8.98 atm (C) 17.06 atm (D) 9.70 atm
- Q.5** Two solutions each in 100 mL having 4 g glucose and 10 g sucrose respectively. How much urea should be added to one of them in order to make them isotonic ?
(A) 0.4218 g urea in glucose solution (B) 0.77 g urea in glucose solution
(C) 0.72 g urea in sucrose solution (D) 0.421 g urea in sucrose solution
- Q.6** 5 g of a polymer of molecular weight 50 kg mol⁻¹ is dissolved in 1 dm³ solution. If the density of this solution is 0.96 kg dm⁻³ at 300 K, the height of solution that will represent this pressure is -
(A) 28.13 mm (B) 20.85 mm (C) 26.52 mm (D) 24.94 mm
- Q.7** 100 mL aqueous solution of glucose with osmotic pressure 1.2 atm at 25°C is mixed with 300 mL aqueous solution of urea at 2.4 atm at 25°C. Osmotic pressure of the mixture is -
(A) 1.37 atm (B) 2.59 atm (C) 1.85 atm (D) 2.13 atm
- Q.8** 10 g of solute A and 20 g of solute B are present in 500 mL of solution. The solution has the same osmotic pressure as 6.67 g of A and 30 g of B present in same volume of solution at same temperature. The ratio of molar masses of solute A and B will be -
(A) 0.25 (B) 0.66 (C) 0.33 (D) 0.75
- Q.9** At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Find out the extent of dilution
(A) 5 (B) 2.5 (C) 1.25 (D) 6.5
- Q.10** The relation ship between osmotic pressure at 273 K, when 10 gm glucose (P₁), 10 gm urea (P₂) and 10 gm sucrose (P₃) are dissolved in 250 ml of water is
(A) P₁ > P₂ > P₃ (B) P₃ > P₁ > P₂ (C) P₂ > P₁ > P₃ (D) P₂ > P₃ > P₁
- Q.11** What osmotic pressure would the 1.25 molal sucrose solution exhibit at 25°C ? The density of this solution is 1.34 g/mL.
(A) 28.70 atm (B) 30.22 atm (C) 21.72 atm (D) 24.55 atm

LIQUID SOLUTIONS

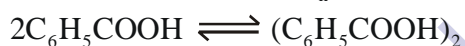
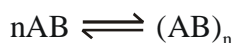
- Q.12** The osmotic pressure of blood is 8.21 atm at 37°C. How much glucose is used per lit for an intravenous injection that is isotonic with blood ?
 (A) 180 gm (B) 342 gm (C) 58.06 gm (D) 55.55 gm
- Q.13** Osmotic pressure of insulin solution at 298 K is found to be 0.0072 atm. Hence, height of water column due to this pressure is [given $d(\text{Hg}) = 13.6 \text{ g/mL}$] –
 (A) 0.760 mm (B) 70.28 mm (C) 74 mm (D) 760 mm
- Q.14** At certain temperature, the osmotic pressure of an aqueous solution of urea was found to be 405 mm. How many times the solution should be diluted in order to exhibit the osmotic pressure of 81 mm at the same temperature ?
 (A) 2 times (B) 4 times (C) 8 times (D) 5 times
- Q.15** If depression in freezing point is 0.93°C then the osmotic pressure of aqueous solution of the given non-electrolyte at 27°C is –
 [Given : K_f for water = 1.86 K kg mol⁻¹ & molality is equal to molarity]
 (A) 12.3 atm (B) 1.23 atm (C) 6.15 atm (D) 2.46 atm

7. Abnormal Molecular Masses

Vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure are colligative properties which depend upon the fraction of solute and solvent particles in solution and not upon the chemical nature of the solute. If solute molecules dissociate in solution, there are more particles in solution and therefore, lowering of vapour pressure shows an increased effect.

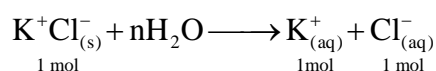


If the solute molecules associate in solution, there are less particles in solution, and therefore lowering of vapour pressure shows a decreased effect.



The molecular mass of a solute is inversely proportional to its molality. If colligative molality is 2 m, the calculated molecular mass is one-half of the actual molecular mass of the solute. If colligative molality is 3 m, the calculated molecular mass is one-third of the actual molecular mass of the solute. The molecular mass of benzoic acid is 122 g/mol. But the molecular mass of benzoic acid dissolved in benzene is found to be 244 g/mol by using a colligative property. Benzoic acid associates to form a dimer and therefore its colligative molality is one-half of the molality of benzoic acid. As molecular mass of a solute is inversely proportional to molality, the molecular mass of benzoic acid determined using a colligative property is double the actual molecular mass of benzoic acid. We can summarize the results as:

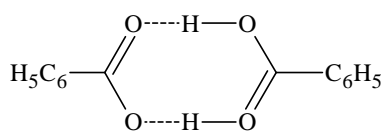
- The extent of dissociation and colligative property.** A solute dissociates completely or partially in solution makes available more particles than would otherwise be present in solution and therefore, a colligative property shows an increased effect. For example, molecular masses obtained of strong acids, bases and salts are much less than their normal values. As an example, one particle of potassium chloride on dissociation in water gives two particles, K^+ and Cl^- and therefore, the molecular mass obtained by a colligative property is half of its normal molecular mass.



- The extent of association and colligative property:** A solute that associates in solution provides less particles that would otherwise be present in solution and therefore, the colligative

LIQUID SOLUTIONS

It is found that compounds which are capable of forming hydrogen bonds, e.g., phenols, carboxylic acids, alcohols: because of association show decreased effect of colligative property.



A dimer of benzoic acid

8. Van't Hoff Factor

In 1886, Van't Hoff, Jacobus Henricus (Dutch chemist, 1859,-1911) introduced a factor 'i' known as Van't Hoff factor to express the extent to association or dissociation of a solute in solution. It can be calculated as:

$$i = \frac{\text{number of solute particles actually present in solution}}{\text{number of solute particles dissolved}}$$

$$= \frac{\text{Observed colligative property}}{\text{normal colligative property}} = \frac{\text{observed molality}}{\text{normal molality}} = \frac{\text{normal molecular weight of solute}}{\text{observed molecular weight of solute}}$$

The Van't Hoff factor for a solute can be calculated by the following modified equations:

$$(i) \quad \frac{P_A^0 - P_A}{P_A^0} = i X_B \quad (ii) \quad \Delta T_f = i K_f m \quad (iii) \quad \Delta T_b = i K_b m \quad (iv) \quad \pi = i CRT$$

where C is molarity of the solution.

Note: For non-electrolytes; $i = 1$

For electrolytes; $i > 1$ (If solute particles undergo Dissociation in the solution)

$i < 1$ (If solute particles undergo Association in the solution)

Application of Van't Hoff Factor:

i) Calculation of Degree of Dissociation of solute particles:

	$A_n \rightleftharpoons nA$	
No. of moles dissolved	1 mol	0
No. of moles after dissociation	$1 - \alpha$	$n\alpha$
Total number of moles present in solution	$= (1 - \alpha) + n\alpha$	

$$\text{Van't Hoff factor, } i = \frac{\text{Moles of solute actually present in solution}}{\text{Moles of solute dissolved}}$$

$$= \frac{(1 - \alpha) + n\alpha}{1} = 1 + (n - 1)\alpha \quad \text{or} \quad \alpha = \frac{i - 1}{n - 1}$$

ii) Calculation of Degree of Association of solute particles: Let n moles of the solute, A, associate to form $(A)_n$. If α is the degree of association.

	$nA \rightleftharpoons A_n$	
No. of moles dissolved	1 mol	0
No. of moles after dissociation	$1 - \alpha$	α/n
Total number of moles present in solution	$= (1 - \alpha) + \alpha/n$	

$$i = \left[1 - \alpha \left(1 - \frac{1}{n} \right) \right] \quad \text{Hence} \quad \alpha = \frac{i - 1}{\frac{1}{n} - 1} = (i - 1) \times \frac{n}{1 - n}$$

LIQUID SOLUTIONS

Illustration 14. A solution is prepared by dissolving 26.3g of CdSO_4 in 1000g water. The depression in freezing point of solution was found to be 0.284K. Calculate the Van't Hoff factor. The cryoscopic constant of water is $1.86\text{K kg solvent mol}^{-1}$ solute.

Solution: Molecular mass $\text{CdSO}_4 = 112.4 + 32 + 4 \times 16 = 208.4 \text{ g/mol}$

$$\begin{aligned}\text{Molality } \text{CdSO}_4 &= \frac{\text{Mass } \text{CdSO}_4}{\text{Molecular mass } \text{CdSO}_4 \times \text{Mass solvent in kg}} \\ &= \frac{26.3\text{g}}{(208.4\text{g/mol}) \times \left(\frac{1000}{1000}\text{kg}\right)} = 0.216\text{m}\end{aligned}$$

$$\Delta T_f = i K_f m \quad \text{or} \quad i = \frac{\Delta T_f}{K_f m} = \frac{0.284\text{K}}{1.86\text{K/m} \times 0.216\text{m}} = 1.21$$

Illustration 15. Three particles of a solute, A, associate in benzene to form species A_3 . Calculate the freezing point of 0.25 molal solution. The degree of association of solute A is found to be 0.80. the freezing point of benzene and its cryoscopic constant are 5.5°C and 5.12 K m^{-1} respectively.

Solution:

	$3A$	\longrightarrow	A_3
No. of moles dissolved	3		0
No. of moles after dissociation	$m(1-\alpha)$		$m\alpha/3$
Total moles present after dissociation			

$$= m(1-\alpha) + m\frac{\alpha}{3} = m\left(1-\alpha + \frac{\alpha}{3}\right) = m\left(1 - \frac{2\alpha}{3}\right) = 0.25\text{m} \left[\frac{3-2 \times 0.8}{3}\right] = 0.177\text{m}$$

$$\Delta T_f = K_f m \quad \text{or} \quad T_f^0 - T_f = 5.12 \text{ K m}^{-1} \times 0.177 \text{ m} = 0.6$$

$$T_f = T_f^0 - 0.6^\circ\text{C} = 5.5^\circ\text{C} - 0.6^\circ\text{C} = 4.9^\circ\text{C}$$

5. Daily Practice Problem Sheet

- Q.1** A pentimolal solution of potassium chloride freezes at -0.68°C . If K_f for H_2O is 1.86, the degree of dissociation of KCl is -
 (A) 75% (B) 83% (C) 65% (D) 92%
- Q.2** The depressions in freezing point of 1 M urea, 1 M glucose and 1 M NaCl are in the ratio :
 (A) 1 : 2 : 3 (B) 3 : 2 : 2 (C) 1 : 1 : 2 (D) none of these
- Q.3** An electrolyte A gives 3 ions and B is a non-electrolyte. If 0.1 M solution of B produces an osmotic pressure P, then 0.05 M solution of A will produce an osmotic pressure, assuming that the electrolyte is completely ionised.
 (A) 1.5 P (B) P (C) 0.5 P (D) 0.75 P
- Q.4** Which is the correct relation between osmotic pressure of 0.1 M NaCl solution and 0.1 M Na_2SO_4 solution ?
 (A) the osmotic pressure of Na_2SO_4 is less than NaCl solution
 (B) the osmotic pressure of Na_2SO_4 is more than NaCl solution
 (C) both have same osmotic pressures
 (D) none of the above
- Q.5** Which one of the following pairs of solutions will be expected to be isotonic under the same temperature?
 (A) 0.1 M urea and 0.1 M NaCl (B) 0.1 M urea and 0.2 M MgCl_2
 (C) 0.1 M NaCl and 0.1 M Na_2SO_4 (D) 0.1 M $\text{Ca}(\text{NO}_3)_2$ and 0.1 M Na_2SO_4

LIQUID SOLUTIONS

- Q.6** The van't Hoff factor of a 0.005 M aqueous solution of KCl is 1.95. The degree of ionisation of KCl is-
 (A) 0.95 (B) 0.97 (C) 0.94 (D) 0.96
- Q.7** What is the freezing point of a solution containing 8.1 g HBr in 100 g water, assuming the acid to be 90% ionised. ? [K_f for water = $1.86 \text{ K kg mol}^{-1}$]
 (A) 0.85°C (B) -3.53°C (C) 0°C (D) -0.35°C
- Q.8** The molal freezing point constant for water is $1.86 \text{ K kg mol}^{-1}$. Therefore, the freezing point of 0.1 M NaCl solution in water is expected to be :
 (A) -1.86°C (B) -0.186°C (C) -0.372°C (D) $+372^\circ\text{C}$
- Q.9** Select correct statement :
 (A) b. p. of 1 molal NaCl solution is twice that of 1 molal sucrose solution
 (B) b. p. elevation of 1 molal glucose solution is half of the 1 molal KCl solution
 (C) b.p. is a colligative property
 (D) all of the above
- Q.10** Two solution of KNO_3 and CH_3COOH are prepared separately molarity of both in 0.1 M and osmotic pressure are P_1 & P_2 . The correct relationship between the osmotic pressure is -
 (A) $P_2 > P_1$ (B) $P_1 > P_2$ (C) $P_1 = P_2$ (D) $\frac{P_1}{P_1 + P_2} + \frac{P_2}{P_1 + P_2}$
- Q.11** A 5.8% wt/vol. NaCl solution will exert an osmotic pressure closest to which one of the following -
 (A) 5.8% (wt/vol) sucrose solution (B) 5.8% (wt/vol) glucose solution
 (C) 2 molal sucrose solution (D) 1 molal glucose solution
- Q.12** How many grams of NaBr must be added to 270 gm of water to lower the vapour pressure by 3.125 mm Hg at temperature at which vapour pressure of water is 50 mm Hg. Assume 100% ionisation of NaBr
 (A) 51.5 gm (B) 103 gm (C) 75 gm (D) 37.5 gm
- Q.13** Sea water is found to contain NaCl & MgCl_2 . If NaCl is 80% ionised and MgCl_2 is 50% ionised then van't Hoff factor is -
 (A) 1.3 (B) 5.0 (C) 3.3 (D) 3.8
- Q.14** The f.p of a 0.08 molal solution of NaHSO_4 is -0.372°C . The dissociation constant for the reaction,
 $\text{HSO}_4^- \longrightarrow \text{H}^+ + \text{SO}_4^{2-}$; is - [K_f for water = 1.86°C]
 (A) 2×10^{-4} (B) 4×10^{-4} (C) 2×10^{-2} (D) 4×10^{-2}
- Q.15** If the observed and normal osmotic pressures of a 1% NaCl solution are 5.75 and 3.00 atm, the degree of dissociation of NaCl is -
 (A) 0.9 (B) 1.0 (C) 0.57 (D) 0.3
- Q.16** 0.01 M solution of KCl and BaCl_2 are prepared in water. The freezing point of KCl is found to be -2°C . What freezing point would you expect for BaCl_2 solution -
 (A) -5°C (B) -4°C (C) -3°C (D) -2°C
- Q.17** The elevation in boiling point of a solution of 10 g of a binary electrolyte (molecular mass 100) in 100 of water is ΔT_b . The value of K_b for water is -
 (A) $\frac{\Delta T_b}{2}$ (B) 10 (C) $10\Delta T_b$ (D) $\frac{\Delta T_b}{10}$
- Q.18** Van't Hoff factors are x, y, z in the case of association, dissociation and no change respectively. Increasing order is -
 (A) $x < y < z$ (B) $x = y = z$ (C) $y < x < z$ (D) $x < z < y$

LIQUID SOLUTIONS

- Q.19** 1 mole each of following solutes are taken in 5 moles water,
(i) NaCl (ii) K_2SO_4 (iii) Na_3PO_4 (iv) glucose
Assuming 100% ionisation of the electrolyte, relative decrease in V. P. will be in order
(A) $i < ii < iii < iv$ (B) $iv < iii < ii < i$ (C) $iv < i < ii < iii$ (D) equal
- Q.20** A 0.002 molar solution of NaCl having degree of dissociation of 90% at 27°C has osmotic pressure equal to -
(A) 0.94 bar (B) 9.4 bar (C) 0.094 bar (D) 9.4×10^{-4} bar
- Q.21** At 20°C, the vapour pressure of 0.1 M solution of urea is 0.0311 mm less than that of water and the vapour pressure of 0.1 M solution of KCl is 0.0574 mm less than that of water. The apparent degree of dissociation of KCl at this dilution is -
(A) 92.1% (B) 84.6% (C) 68.4% (D) 54.1%
- Q.22** The freezing point of a solution of 20.5 g NH_4Br in 100 g of water is $-6.2^\circ C$. The freezing point of a solution of 3.42 g cane-sugar in 100 g of water is $-0.185^\circ C$. The degree of ionisation of salt is -
(A) 80% (B) 30% (C) 60% (D) 40%
- Q.23** A 1.2% solution (wt./ volume) of NaCl is isotonic with 7.2% solution (wt. /volume) of glucose. Degree of ionisation and van't Hoff factor of NaCl is -
(A) $\alpha = 95\%$, $i = 1.95$ (B) $\alpha = 90\%$, $i = 1.90$
(C) $\alpha = 85\%$, $i = 1.85$ (D) $\alpha = 75\%$, $i = 1.75$
- Q.24** 1 g of monobasic acid in 100 g of water lowers the freezing point by 0.168° . If 0.2 g of same acid requires 15.1 mL of N/10 alkali for complete neutralization, degree of dissociation of acid will be -
[K_f for H_2O is $1.86 K mol^{-1} kg$]
(A) 16.8% (B) 22.4% (C) 19.6% (D) 26.2%
- Q.25** The molal depression of the freezing point in 1000 g of water is 1.86. What would be the depression of freezing point of water when :
(i) 120 g of urea is dissolved in 1000 gm of water.
(A) $1.86^\circ C$ (B) $8.26^\circ C$ (C) $7.87^\circ C$ (D) $3.72^\circ C$
(ii) 117 g of sodium chloride is dissolved in 1000 gm of water (Assuming sodium chloride is fully ionised)
(A) $7.44^\circ C$ (B) $3.72^\circ C$ (C) $11.16^\circ C$ (D) $6.18^\circ C$
(iii) 488.74 g of $BaCl_2 \cdot 2H_2O$ have been dissolved in 1000 g of water. (Assuming barium chloride is fully ionised)
(A) $7.44^\circ C$ (B) $11.16^\circ C$ (C) $3.72^\circ C$ (D) $5.87^\circ C$

ANSWERS

1. Daily Practice Problem Sheet

- | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (A) | 2. (C) | 3. (A) | 4. (B) | 5. (C) | 6. (B) | 7. (A) |
| 8. (A) | 9. (B) | 10. (A) | 11. (A) | 12. (C) | 13. (C) | 14. (B) |
| 15. (C) | 16. (B) | 17. (B) | 18. (A) | 19. (A) | | |

2. Daily Practice Problem Sheet

- | | | | | | | |
|--------------------------------|---------|---------|---------|---------|----------------------|---------|
| 1. (B) | 2. (C) | 3. (C) | 4. (D) | 5. (B) | 6. (B) | 7. (C) |
| 8. (C) | 9. (B) | 10. (A) | 11. (B) | 12. (C) | 13. (i) (A) (ii) (D) | |
| 14. (C) | 15. (A) | 16. (D) | 17. (A) | 18. (D) | 19. (C) | 20. (B) |
| 21. (A) | 22. (A) | 23. (D) | 24. (A) | 25. (D) | 26. (C) | |
| 27. (i) (A) (ii) (D) (iii) (B) | | | 28. (A) | 29. (C) | 30. (A) | |

3. Daily Practice Problem Sheet

- | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (C) | 2. (B) | 3. (D) | 4. (D) | 5. (B) | 6. (B) | 7. (C) |
| 8. (A) | 9. (B) | 10. (B) | 11. (C) | 12. (A) | 13. (A) | 14. (C) |
| 15. (B) | 16. (D) | 17. (B) | 18. (C) | 19. (C) | 20. (D) | |

4. Daily Practice Problem Sheet

- | | | | | | | |
|---------|--------|---------|---------|---------|---------|---------|
| 1. (C) | 2. (B) | 3. (A) | 4. (D) | 5. (A) | 6. (C) | 7. (D) |
| 8. (C) | 9. (A) | 10. (C) | 11. (A) | 12. (C) | 13. (C) | 14. (B) |
| 15. (A) | | | | | | |

5. Daily Practice Problem Sheet

- | | | | | | | |
|---------|---------|---------|--------------------------------|---------|---------|---------|
| 1. (B) | 2. (C) | 3. (A) | 4. (B) | 5. (D) | 6. (A) | 7. (B) |
| 8. (C) | 9. (B) | 10. (D) | 11. (C) | 12. (A) | 13. (C) | 14. (D) |
| 15. (A) | 16. (C) | 17. (A) | 18. (D) | 19. (C) | 20. (C) | 21. (B) |
| 22. (C) | 23. (A) | 24. (C) | 25. (i) (D) (ii) (A) (iii) (B) | | | |

SOLVED PROBLEMS

SUBJECTIVE

Problem 1: Calculate the molecular weight of cellulose acetate if its 0.5% (wt./vol) solution in acetone (sp. gr. = 0.9) shows an osmotic rise of 23 mm against pure acetone at 27°C.

Solution: 0.5% (wt./vol) solution means 0.5 gm of cellulose acetate is dissolved in 100 ml solution.
Osmotic pressure = 23 mm of pure acetone

$$\pi = 2.3 \text{ Cm of pure acetone} = \frac{2.3 \times 0.9}{13.6} \text{ cm of Hg} = 0.1522 \text{ cm of Hg}$$

$$\pi = \frac{0.1522}{76} \text{ atm} = 0.002 \text{ atm}$$

$$\text{Let the molecular weight of the cellulose acetate be } M \Rightarrow n_{\text{cellulose acetate}} = \frac{0.5}{M}$$

$$\text{Volume} = v = 100 \text{ ml} = 0.1 \text{ lit}$$

$$R = 0.082 \text{ lit atm mol}^{-1} \text{ K}^{-1}, T = (27 + 273) = 300 \text{ K}$$

$$\pi = \frac{n}{v} \times RT \Rightarrow 0.002 = \frac{0.5}{M} \times \frac{1}{0.1} \times 0.0821 \times 300 \quad \therefore M = 61575$$

Problem 2: 1kg of an aqueous solution of Sucrose is cooled and maintained at -4°C. How much ice will be separated out if the molality of the solution is 0.75? $K_f(\text{H}_2\text{O}) = 1.86 \text{ Kg mol}^{-1}\text{K}$.

Solution: Since molality of solution is .75 ,
hence .75 moles of sucrose are present in 1000 g of solvent (i.e. water)

$$\square m_{\text{solution}} = m_{\text{water}} + m_{\text{sucrose}} = 1000 + .75 \times 342 = 1256.5 \text{ gm}$$

$$\therefore m_{\text{sucrose}} \text{ (in kg)} = \frac{256.5}{1256.5} \times 1000 = 204.14 \text{ gm}, \quad m_{\text{water}} = 1000 - 204.14 = 795.86 \text{ gm}$$

$$\square \Delta T_f = K_f \times m \Rightarrow 4 = 1.86 \times \frac{204.14 / 342}{W / 1000} \Rightarrow w = 277.15$$

$$\therefore \text{amount of ice} = 795.86 - 277.15 = 518.31 \text{ gm}$$

Problem 3: River water is found to contain 11.7% NaCl, 9.5% MgCl_2 , and 8.4% NaHCO_3 by weight of solution. Calculate its normal boiling point assuming 90% ionization of NaCl, 70% ionization of MgCl_2 and 50% ionization of NaHCO_3 (K_b for water = 0.52)

$$\text{Solution: } n_{\text{NaCl}} = \frac{11.7}{58.5} = 0.2, \quad n_{\text{MgCl}_2} = \frac{9.5}{95} = 0.1, \quad n_{\text{NaHCO}_3} = \frac{8.4}{84} = 0.1$$

$$i_{\text{NaCl}} = 1 + \alpha = 1 + 0.9 = 1.9,$$

$$i_{\text{MgCl}_2} = 1 + 2\alpha = 1 + 0.7 \times 2 = 2.4,$$

$$i_{\text{NaHCO}_3} = 1 + \alpha = 1 + 0.5 \times 2 = 2.0$$

$$\text{Weight of solvent} = 100 - (11.7 + 9.5 + 8.4) = 70.4 \text{ g}$$

$$\Delta T_b = \frac{(i_{\text{NaCl}} \times n_{\text{NaCl}} + i_{\text{MgCl}_2} \times n_{\text{MgCl}_2} + i_{\text{NaHCO}_3} \times n_{\text{NaHCO}_3}) \times K_b \times 1000}{\text{Weight of solvent}}$$

$$= \frac{(1.9 \times 0.2 + 2.4 \times 0.1 + 2 \times 0.1) \times 0.52 \times 1000}{70.4} = 5.94^\circ\text{C}$$

$$\therefore \text{Boiling point of solution} = 100 + 5.94 = 105.95^\circ\text{C}$$

LIQUID SOLUTIONS

Problem 4: An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition $C_xH_{2x}O_x$ in 90 gm water boils at 101.24°C at 1.00 atmospheric pressure. What is the molecular formula?

$$K_b(H_2O) = 0.512 \text{ K mol}^{-1} \text{ kg } T_b(H_2O) = 100^\circ\text{C}$$

Solution: Elevation in B.P. = $101.24 - 100 = 1.24^\circ\text{C}$

$$\Delta T_b = K_b \times i \times \text{molality} \Rightarrow 1.24 = 0.512 \times \frac{288}{m} \times \frac{1000}{90} \quad (\therefore i = 1)$$

$$\therefore m = 1321.2 \text{ gm mol}^{-1}$$

$$\text{molar mass of } C_xH_{2x}O_x = 12x + 1 \times 2x + 16x = 30x$$

$$\therefore 30x = 1321.2 \quad \therefore x = 44 \quad \text{Hence the molecular formula is } = C_{44}H_{88}O_{44}$$

Problem 5: 30 ml of CH_3OH ($d = 0.7980 \text{ gm cm}^{-3}$) and 70 ml of H_2O ($d = 0.9984 \text{ gm cm}^{-3}$) are mixed at 25°C to form a solution of density $0.9575 \text{ gm cm}^{-3}$. Calculate the freezing point of the solution. $K_f(H_2O)$ is $1.86 \text{ K kg mol}^{-1}$. Also calculate its molarity

Solution: Weight of CH_3OH (w_1) = $30 \text{ cm}^3 \times 0.7980 \text{ gm/cm}^3 = 23.94 \text{ gm}$

$$\text{Weight of solvent } (H_2O) \text{ } (w_2) = 70 \text{ cm}^3 \times 0.9984 \text{ gm cm}^3 = 69.888 \text{ gm}$$

$$m = \frac{23.94}{32} \times \frac{1000}{69.88} = 10.7046 \text{ molal}$$

$$\therefore \Delta T_f = K_f \times i \times \text{molality}, \quad (\text{for } CH_3OH, i = 1)$$

$$\Delta T_f = 1.86 \times 10.7046^\circ\text{C} = 19.91^\circ\text{C}$$

$$\text{Freezing point of the solution} = 0 - 19.91^\circ\text{C} = -19.91^\circ\text{C}$$

$$\text{Weight of solution} = \text{weight of solute} + \text{weight of solvent} = 23.94 + 69.888 = 93.828 \text{ gm}$$

$$\text{volume of the solution} = \frac{\text{wt. of the solution}}{\text{density of the solution}} = \frac{93.828}{0.95751} = 97.99 \text{ ml}$$

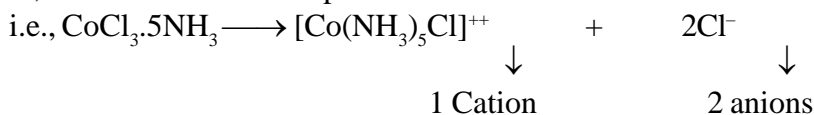
$$M (\text{molarity}) = \frac{23.94}{32} \times \frac{1000}{97.99} \text{ mol lit}^{-1} = 7.63 \text{ M}$$

Problem 6: A complex is represented as $CoCl_3 \cdot xNH_3$. Its 0.1 m solution in aqueous solution shows $\Delta T_f = 0.558^\circ\text{C}$, $K_f(H_2O) = 1.86 \text{ mol}^{-1} \text{ K}$ and assume 100% ionization and co-ordination number of Co(III) is six. What is the complex?

Solution: $\Delta T_f = i \times K_f \times m, \quad \Rightarrow 0.558 = 1.86 \times 0.1 \times i$

$$\therefore i = \frac{0.558}{0.186} = 3$$

or, $i \approx 3$ indicates that complex ionize to form three ions since co-ordination number is 6 hence $x = 5$



So, the complex is $[Co(NH_3)_5Cl]Cl_2$

Problem 7: A solution comprising 0.1 mol of naphthalene and 0.9 mol of benzene is cooled until some benzene freezes out. The solution is then decanted off from the solid and warmed to 353 K, where its vapour pressure is found to be 670 torr. The freezing and normal boiling point of benzene are 278.5 K and 353 K, respectively. Calculate the temperature to which the solution was cooled originally and the amount of benzene that must have frozen out. Assume conditions of ideal solution. K_f for benzene = 5 K kg mole^{-1} .

LIQUID SOLUTIONS

Solution: Molality of the resulting solution (i.e. after the benzene freezes out) can be determined on the basis Raoult's law.

$$m = \frac{X_{\text{naph}} \times 1000}{X_{\text{benzene}} \times 78} = \frac{(760 - 670)}{0.88 \times 78} = 1.72 \text{ mol kg}^{-1}.$$

$$\text{Weight of benzene in the resulting solution} = \left(\frac{1000}{1.72} \times 0.1 \right) = 58.1 \text{ g}$$

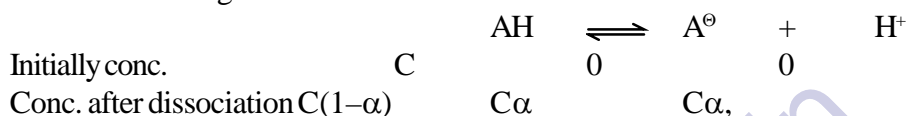
$$\text{Amount of benzene frozen} = 0.9 \times 78 - 58.1 = 12.1 \text{ g}$$

$$\Delta T_f = K_f m = 5 \times 1.72 = 8.60 \text{ K}$$

$$\text{Hence the temp to which the solution was cooled} = 278.5 - 8.60 = 269.9 \text{ K}$$

Problem 8: Find K_a , the ionization constant of tartaric acid if a 0.100 molal aqueous solution of tartaric acid freezes at -0.205°C . Assume that only the first ionization is of importance and that $0.1 \text{ m} = 0.1 \text{ M}$. $K_f = 1.86 \text{ kg mol}^{-1} \text{ K}$.

Solution: Assuming that the tartaric acid be a monobasic as AH. It ionizes as



$$\text{Here, } i = \frac{C(1-\alpha) + C\alpha + C\alpha}{C}, \text{ where } \alpha = \text{degree of dissociation} = \frac{C(1+\alpha)}{C} = 1+\alpha$$

$$\text{Molal concentration} = 0.1$$

$$\Delta T_f = K_f \times C_m \times i \quad \Rightarrow \quad 0.205 = 1.86 \times 0.1 \times (1+\alpha) \quad \therefore \alpha = 0.1$$

$$K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{AH}]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{\alpha^2 C}{1-\alpha} \quad K_a = \frac{(0.1)^2 \times 0.1}{1-0.1} = 1.11 \times 10^{-3}$$

$$\therefore K_a = 1.11 \times 10^{-3}$$

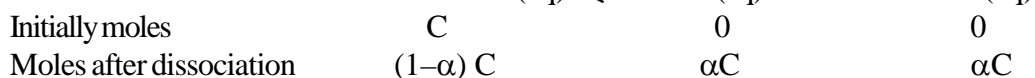
Problem 9: The freezing point depression of a 0.109 M aq. solution of formic acid is -0.21°C .

Calculate the equilibrium constant for the reaction,



K_f for water = $1.86 \text{ kg mol}^{-1} \text{ K}$

Solution:



$$i = \frac{(1-\alpha) \times C + \alpha \times C + \alpha \times C}{1 \times C} = 1 + \alpha,$$

$$\Delta T_f = K_f \times i \times C_m$$

$$0.21 = 1.86 \times (1+\alpha) \times 0.109 \text{ (for dilute solution molality } \approx \text{ molarity)}$$

$$\therefore 1+\alpha = \frac{0.21}{1.86 \times 0.109} = 1.0358 \quad \Rightarrow \quad \alpha = 0.0358 = 0.036$$

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.109 \times (0.036)^2}{0.964} = 1.41 \times 10^{-5}$$

LIQUID SOLUTIONS

Problem 10: The freezing point of a solution of acetic acid (mole fraction is 0.02) in benzene 277.4 K. Acetic acid exists partly as a dimer $2A \rightleftharpoons A_2$. Calculate equilibrium constant for dimerisation. Freezing point of benzene is 278.4 K and (K_f for benzene is 5)

Solution:

$2A$	\rightleftharpoons	A_2	
1		0	initially moles
$1-\alpha$		$\alpha/2$	moles after dimer is formed

$$\therefore i = \frac{(1-\alpha) + \alpha/2}{1} = 1 - \alpha/2$$

$$X_A = 0.02, \quad X_B = 0.98$$

$$\text{Molality of A in B} = \frac{x_A}{m_B} \times \frac{1000}{X_B} = \frac{0.02}{78} \times \frac{1000}{0.98} = 0.262 \text{ mol kg}^{-1} \text{ of Benzene}$$

$$\text{Since, } \Delta T_f = K_f \times i \times \text{molality} \quad 278.4 - 277.4 = 5 \times i \times 0.262$$

$$\text{or, } 1 = 5 \times i \times 0.262, \quad i = \frac{1}{5 \times 0.262} = 0.763, \quad 1 - \alpha/2 = 0.763 \Rightarrow \alpha = 0.47$$

Hence the molality of A after dimer is formed = $(1-\alpha) \times \text{initial molality}$

$$= (1 - 0.48) \times \text{initial molality} = 0.52 \times 0.262$$

Molality of A_2 after dimer is formed

$$= \frac{\alpha}{2} \times \text{molality} = \frac{0.48}{2} \times 0.262 = 0.24 \times 0.26 = 0.06288$$

$$\text{The equilibrium constant} \quad K_{eq} = \frac{[A_2]}{[A]^2} = \frac{0.06288}{(0.13624)^2} = 3.39 \text{ kg mol}^{-1}$$

OBJECTIVE

Problem 1: A weak electrolyte, AB, is 5% dissociated in aqueous solution. What is the freezing point of a 0.100 molal aqueous solution of AB? K_f for water is 1.86 deg/molal.

- (A) -3.8°C (B) -0.1953°C (C) -1.7°C (D) -0.78°C

Solution: Ans (b)

$$\text{For AB, } n = 2 \quad \therefore i = 1 + (2-1)\alpha = 1 + \alpha = 1.05$$

$$\therefore \Delta T_f = i \times X_f \times m = 1.05 \times 1.86 \times .1 = .1953 \quad \therefore T_f = - .1953^\circ\text{C}$$

Problem 2: Calculate the boiling point of a one molar aqueous solution (density = 1.04 g mL^{-1}) of potassium chloride, K_b for water = 0.52 kg mol^{-1} . Atomic masses of K = 39, Cl = 35.5

- (A) 107.28°C (B) 103.68°C (C) 101.078°C (D) None of these

Solution: Ans. (c)

$$m = \frac{1000 \times 1}{1000 \times 1.04 - 1 \times 74.5} = 1.036$$

$$\Delta T_b = 1 \times X_b \times m \Rightarrow \Delta T_b = 2 \times 0.52 \times 1.036 = 1.078 \Rightarrow T_b = 101.078^\circ\text{C}$$

(KCl is an electrolyte having $n = 2$, $\alpha = 1$ (if not given))

Problem 3: The vapour pressure of a solvent decreased by 10 mm Hg when a non volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg.

- (A) 0.8 (B) 0.6 (C) 0.4 (D) 0.2

Solution: Ans.: (b)

$$P^0 - P_s = P^0 \times X_B \quad 10 = P^0 \times 0.2$$

$$\text{Again, } 20 = P^0 \times X_B \quad \text{Hence, } n = 0.4,$$

$$\text{so, mole fraction of solvent} = 1 - 0.4 = 0.6$$

LIQUID SOLUTIONS

Problem 4: The molal freezing point constant for water is $1.86 \text{ K} \cdot \text{molality}^{-1}$. If 34.2 g of cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) are dissolved in 1000 g of water, the solution will freeze at
 (A) -1.86°C (B) 1.86°C (C) -3.92°C (D) 2.42°C

Solution: Ans.: (a)

$$\Delta T_f = \frac{1000 \times K_f \times w}{\text{MW}} = \frac{1000 \times 1.86 \times 34.2}{100 \times 342} = 1.86^\circ \quad \therefore T_f = 0 - 1.86 = -1.86^\circ \text{C}$$

Problem 5: 20 g of a binary electrolyte (mol. wt. = 100) are dissolved in 500 g of water. The freezing point of the solution is -0.74°C , $K_f = 1.86 \text{ K} \cdot \text{molality}^{-1}$. The degree of ionisation of the electrolyte is
 (A) 50% (B) 75% (C) 100% (D) 0

Solution: Ans.: (d)

$$\Delta T_f = i \times X_f \times m \quad \Rightarrow .74 = (1 + \alpha) \times \frac{20/100}{500/1000} \quad \Rightarrow 1 + \alpha = 1 \quad \Rightarrow \alpha = 0$$

Problem 6: $Y \text{ g}$ of non - volatile organic substance of molecular mass M is dissolved in 250 g benzene. Molal elevation constant of benzene is K_b . Elevation in its boiling point is given by

(A) $\frac{M}{K_b Y}$ (B) $\frac{4K_b Y}{M}$ (C) $\frac{K_b Y}{4M}$ (D) $\frac{K_b Y}{M}$

Solution: Ans.: (b) $\Delta T = \frac{1000 \times K_b \times Y}{250 \times M} = \frac{4K_b Y}{M}$

Problem 7: The values of observed and calculated molecular weights of silver nitrate are 92.64 and 170 respectively. The degree of dissociation of silver nitrate is
 (A) 60% (B) 83.5% (C) 46.7% (D) 60.23%

Solution: Ans.: (b) i for $\text{AgNO}_3 = \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = 1 + \alpha \Rightarrow \alpha = \frac{170}{92.64} - 1 = 0.835 = 83.5 \%$

Problem 8: At 40°C , the vapour pressures in torr, of methyl alcohol - ethyl alcohol solution is represented by the equation. $P = 119X_A + 135$ where X_A is mole fraction of methyl alcohol, then the value of

$$\lim_{X_A \rightarrow 1} \frac{P_A}{X_A} \text{ is}$$

(A) 254 torr (B) 135 torr (C) 119 torr (D) 140 torr

Solution: Ans.: (a) $P = 119X_A + 135$; $\lim_{X_A \rightarrow 1} \frac{P_A}{X_A} = 119 + 135 = 254$

Problem 9: The amount of ice that will separate on cooling a solution containing 50 g of ethylene glycol in 200 g water to -9.3°C is : [$K_f = 1.86 \text{ K} \cdot \text{molality}^{-1}$]
 (A) 38.71 g (B) 38.71 mg (C) 42 g (D) 42 mg

Solution: Ans.: (a)

$$\Delta T = \frac{1000 \times K_f \times w}{W \times M} \Rightarrow 9.3 = \frac{1000 \times 1.86 \times 50}{62 \times W} \Rightarrow \therefore W = 161.29$$

$\therefore \text{Ice separated} = 200 - 161.29 = 38.71 \text{ g}$