CHAPTER / 02

Solutions

Topics Covered

Types of Solution, Expressing Concentration of Solutions

- Types of Solution
- Expressing Concentration of Solutions

Solubility

- Solubility of Solute in Solvent
- Solubility of Gases in Liquids
- Henry's Law

Vapour Pressure of Liquid Solution Ideal and Non-ideal Solutions

Vapour Pressure

Raoult's Law

Ideal and Non-ideal Solutions
Colligative Properties and
Determination of Molecular Mass

van't Hoff Factor

Solutions are homogeneous mixtures of two or more than two components. The substances forming the solution are called components of the solution. The component present in smaller amount is called **solute** and the other present in larger amount in which solute is dissolved, is called **solvent**. The solutions containing two components are binary solutions, e.g. salt solution.

TOPIC ~01 Types of Solution, Expressing Concentration of Solutions

Types of Solution

Solutions are classified into different types on the following basis :

On the Basis of Solvent

On the basis of solvent, the solution may be of the following types:

- (i) **Aqueous solution** When solute is dissolved in water, it is known as aqueous solution, e.g. ethanol in water.
- (ii) **Non-aqueous solution** When solute is dissolved in a solvent other than water, it is known as non-aqueous solution, e.g. iodine in alcohol (tincture of iodine).

On the Basis of Quantity of Solute

On the basis of quantity of solute, the solution may be of following types:

- (i) **Saturated solution** The solution containing the maximum possible quantity of solute dissolved in a solvent at a certain temperature is called saturated solution.
- (ii) Unsaturated solution The solution having lower quantity of solute than saturated solution dissolved in the solvent is called unsaturated solution. It can be further divided into two types.
 - (a) **Dilute solution** Solution containing lower quantity of solute.
 - (b) **Concentrated solution** Solution containing higher quantity of solute but still lower than the quantity of a saturated solution.
- (iii) **Supersaturated solution** At constant temperature, when the quantity of solute is greater than that in saturated solution then solution is known as supersaturated solution.

On the Basis of Physical State of Component

On the basis of physical state of components, i.e. solute and solvent, solution can be broadly divided into three types. Their further subdivisions and examples are tabulated below:

Types of Solutions	Solute	Solvent	Examples
Solid solutions	Gas	Solid	Hydrogen in palladium.
	Liquid	Solid	Mercury with sodium forming an amalgam.
	Solid	Solid	Alloys like bronze and many others.
Liquid solutions	Gas Liquid O: dr		Oxygen in water, aerated drinks, carbon dioxide in water.
	Liquid	Liquid	Alcoholic beverages are basically solutions of ethanol in water.
	Solid	Liquid	Sucrose (table sugar) or salt in water.
Gaseous solutions	s Gas Gas n s Liquid Gas		Air which is mostly mixture of nitrogen and oxygen gases.
			Chloroform mixed with nitrogen gas, humidity in air.
	Solid	Gas	Camphor in nitrogen gas, dust or smoke. Adsorption of gases over metal

Expressing Concentration of Solutions

Concentration of a solution may be defined as the amount of solute present in the given quantity of the solution.

Several methods by which we can describe concentration of the solution are as follows :

1. Mass per cent (w/w)

The mass percentage of a component in a given solution is the mass of the component per 100 g of the solution. . . .

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

2. Volume per cent (V/V)

The volume percentage is the volume of the component per 100 parts by volume of the solution.

Volume per cent = $\frac{\text{Volume of the component}}{\text{Total volume of the solution}} \times 100$

3. Mass by Volume Percentage (w/V)

Mass by volume percentage is the mass of solute dissolved in 100 mL of the solution.

Mass by volume % =
$$\frac{\text{Mass of the solute}}{\text{Volume of the solution}} \times 100$$

4. Mole Fraction (χ)

It is the ratio of number of moles of one component to the total number of moles of all the components present in the solution. For a binary solution having solvent 1 and solute 2, then Mole fraction of solute,

$$\chi_2 = \frac{n_2}{n_1 + n_2}$$

Similarly, mole fraction of solvent,

$$\chi_1 = \frac{n_1}{n_1 + n_2}$$

 $\chi_1 + \chi_2 = 1$ Mole fraction of solution containing 'i' number of components,

$$\chi_i = \frac{n_i}{n_1 + n_2 + n_3 + \dots + n_i} = \frac{n_i}{\Sigma n_i}$$

5. Parts Per Million (ppm)

When a solute is present in trace quantities, the concentration is expressed in parts per million (ppm).

Parts per million

:..

Number of parts of the component $\times 10^6$

Total number of parts of all the components of the solution

6. Molarity (M)

It is defined as the number of moles of solute dissolved in one litre (or one cubic decimetre) of the solution.

Molarity
$$(M) = \frac{\text{Number of moles of solute} \times 1000}{1000}$$

Volume of solution (mL)
(Moles of solute =
$$\frac{W_2}{M_2}$$
, where W_2 = mass of solute(g)
and M_2 = molar mass of solute)

$$Volume = \frac{Mass}{Density}$$

Molarity is a function of temperature and changes with change in temperature because volume depends upon temperature.

7. Molality (m)

It is defined as the number of moles of solute per kilogram of the solvent.

Molality
$$(m) = \frac{\text{Number of moles of solute} \times 1000}{\text{Mass of solvent } (g)}$$

8. Normality (N)

It is the number of gram equivalents of the solute dissolved in one litre of the solution.

Normality

$$(N) = \frac{\text{Number of gram equivalents of solute} \times 1000}{\text{Volume of solution (mL)}}$$
(Gram equivalents of solute = $\frac{W_2}{\text{Equivalent weight}}$

where, $W_2 = mass$ of solute and

equivalent weight = $\frac{\text{molecular mass}}{1}$ valencv

9. Formality

This is the concentration unit for ionic compounds. It represents number of gram formula weight of the substance dissolved per litre of the solution.

Formality

Moles of substance added to solutions

Volume of solution (mL)

Mass of solute
$$(g) \times 1000$$

Formula mass of solution $(g) \times Volume of solution (mL)$

Relation between Different Concentration Terms

Various expressions for concentration of solutions can be related as given below:

(i) Relation between molality (m) and mole fraction (γ)

 $\chi = \frac{m M_1}{(1000 + m M_1)} \quad \text{or} \quad m = \frac{1000\chi}{(1 - \chi)M_1}$

where, M_1 = molecular mass of the solvent

(ii) Relation between molality (m) and molarity (M)

Molality $(m) = \frac{m}{d - MM_2}$ (If d in kg L⁻¹ and M_2 in kg mol⁻¹)

Molality
$$(m) = \frac{1}{1000d - MM_2} \times 1000$$

(If d in g mL⁻¹ and M_2 in g mol⁻¹)

Molarity
$$(M) = \frac{m \times d}{1 + \frac{m \times M_2}{1000}}$$

where,
$$M_2 = \text{molar mass of the solute}$$

 $d = \text{density of the solution}$

(iii) Relation between normality (N) and strength in gL^{-1}

$$N = \frac{x \times d \times 10}{E}$$

where, x = % of the solute by mass $d = \text{density of solution in g mL}^{-1}$ E = equivalent mass of solute

- (iv) Relation between molarity and strength in g/L
 - Weight of solute (in g) Molarity (M) =Molecular weight of solute \times volume of solution (in L)

Molarity
$$(M) = \frac{\text{Strength in g } L^{-1}}{\text{Molecular weight of solute}}$$

(v) Relation between normality and molarity

 $\frac{Normality}{Molarity} = \frac{Molecular \ weight}{Equivalent \ weight}$

- For an acid, $\frac{\text{Molecular weight}}{\text{Equivalent weight}} = \text{basicity}$
- :. Normality of an acid = molarity × basicity $\underline{\text{Molecular weight}}_{=} = \text{acidity}$ For a base, $\frac{100000000}{\text{Equivalent weight}}$

 \therefore Normality of a base = molarity × acidity

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK Questions

Exams' Questions

Q.1 What is molarity of 10% NaOH (w/v) solution? [2018]

(a) 4.5 mol L^{-1} (c) 2.5 mol L^{-1}

(b) $3.5 \text{ mol } L^{-1}$ (d) $2.8 \text{ mol } \text{L}^{-1}$

Sol. (c) Given, $w_{\!B}=10~{\rm g}$

 $w_A = 100 \text{ mL}$

10% NaOH (w/v) solution means 10 g of NaOH dissolved in 100 mL of solution.

We know that, number of moles of NaOH

$$= \frac{\text{Weight of NaOH}}{\text{Molar mass of NaOH}}$$
$$= \frac{10 \text{ g}}{40 \text{ g mol}^{-1}}$$
Thus, molarity =
$$\frac{\text{Number of moles of NaOH}}{\text{Volume of solution (in L)}}$$
$$= \frac{10 \text{ g}}{40 \text{ g mol}^{-1}} \times \frac{1000 \text{ mL L}^{-1}}{100 \text{ mL}} = \frac{10}{4}$$
$$= 2.5 \text{ mol L}^{-1}$$

Important Questions

- Q.2 Glucose solution is 25% by weight of solution. Its per cent concentration by weight of solvent is (a) 20% (b) 25% (c) 33.3% (d) 16.66%
- Sol. (c) Per cent concentration by weight of solvent $= \frac{\text{weight of solute}}{\text{weight of solvent}} \times 100 = \frac{25}{75} \times 100 = 33.3\%$
- Q.3 Mole fraction of the solute in a 1.00 molal aqueous solution is
 - (a) 1.7700 (b) 0.1770 (c) 0.0177 (d) 0.0344
- Sol. (c) Molality is number of moles of solute dissolved in the 1 kg of solvent. Therefore, 1 molal aqueous solution means 1 mole of solute present in 1 kg of water.
 - Molecular mass of water = 18 g/mol

Given, mass of water = 1 kg

: Number of moles =
$$\frac{1000}{18}$$
 = 55.5 moles

Mole fraction of solute

$$= \frac{\text{Moles of solute}}{\text{Total number of moles in solution}}$$
$$= \frac{1}{56.5} = 0.0177$$

- Q.4 Mole fraction of a solute in benzene is 0.2 then what is the value of molality of solute?
 - (a) 3.2 (b) 2 (c) 4 (d) 3.6
- **Sol.** (a) Let the molality of solution be x.

 \therefore Moles of benzene present in 1000 g of benzene

$$= \frac{1000}{78} = 120.82$$

$$\therefore \text{ Mole fraction of solute} = \frac{x}{x+12.82} \text{ or } 0.2 = \frac{x}{x+12.82}$$

$$\therefore \qquad x = 3.2$$

x = 3.2

- Q.5 Which of the following concentration terms is/are independent of temperature?
 - (a) Molality
 - (b) Molality and mole fraction
 - (c) Molarity and mole fraction
 - (d) Molality and normality
- Sol. (b) Molality and mole fraction are temperature independent entities.
- Q.6. An example of a solid solution in which the solute in a gas is
- Sol. Solution of hydrogen (solute) in palladium (solvent).

Q.7 12 g of H_2SO_4 is dissolved in water to make

1200 mL of the solution.	The concentration in
normality is	[Textbook]
(a) 0.051	(b) 0.102
(c) 0.122	(d) 0.204

Sol (d) Given,
$$w_B = 12$$
 g
Volume of solution = 1200 mL or 1.2 L
 $M_B = 98$ g mol⁻¹
Equivalent weight of $H_2SO_4 = \frac{98}{2} = 49$ g eq.
Normality = $\frac{No. \text{ of gram equivalents}}{Volume of solution (in L)} = \frac{\frac{12}{49}}{1.2} = 0.204 \text{ N}$
Q.8 The normality of 26.5 g of Na₂CO₃ present in
one kilolitre solution is [Textbook]
(a) 0.25 N (b) 0.05 N
(c) 0.5 N (d) None of these
Sol (d) Given, $w_B = 265$ g
Volume = 10^3 L
Equivalent weight of Na₂CO₃ = $\frac{M. \text{ Wt}}{\text{Charge}} = \frac{105.98}{2} = 53$
Normality = $\frac{\text{Number of gram equivalents}}{\text{Volume of solution (in L)}} = \frac{\frac{26.5}{53}}{10^3}$
= 0.0005 N
Q.9 The molarity of pure water is [Textbook]
(a) 55.6 (b) 50 (c) 100 (d) 18
Sol (a) Molarity is defined as the number of moles of

Sol (a) Molarity is de solute present per litre of solution. As in 1 L of water, $\frac{1000}{18}$ moles of water are present, i.e.

= 55.6 moles of water

Thus, the molarity of pure water is 55.6 M.

Q.10 5.85 g of NaCl is dissolved in 90 g of water. The mole fraction of the solute is (a) 0.01 (b) 0.1 (c) 0.2 (d) 0.0196

Sol (d) Given, $w_B = 5.85 \text{ g} \Rightarrow w_A = 90 \text{ g}$

$$M_B = 58.5 \text{ m mol}^{-1}, \ M_A = 18 \text{ g mol}^{-1}$$
$$\therefore \ \chi_B = \frac{n_B}{n_A + n_B} = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}} = \frac{\frac{5.85}{58.5}}{\frac{5.85}{58.5} + \frac{90}{18}} = \frac{0.1}{5.1} = 0.0196$$

2 MARK Questions

Exams' Questions

- Q.11 A solution contains 72% water and 28% methyl alcohol. Calculate the mole fraction of each component in the solution. [2019]
- Sol If solution has 72% H₂O by mass and 28% CH₃OH by mass, then mass of H_2O in 100 g of solution = 72 g and moles (*n*) of $H_2O = \frac{72}{18} = 4.00$ mol

Mass of CH₃OH in 100 g of solution=28 g (:: Molar mass of $CH_3OH = 32$) \therefore Moles (n) of CH₃OH = $\frac{28}{32}$ = 0.88 mol :. Total moles = 4.0 + 0.88 = 4.88 = 4.88 mol Hence, mole fraction of $H_2O = \frac{Moles \text{ of } H_2O}{Total \text{ moles}} = \frac{4.0}{4.88}$ $-\frac{1}{4.88}$ =0.82Mole fraction of water = 0.82:. Mole fraction of $CH_3OH = 1 - 0.82 = 0.18$ (2) **Q.12** 50 mL of $\frac{N}{10}$ NaOH solution, 100 mL of $\frac{N}{5}$ NaOH solution and 500 mL of $\frac{N}{2}$ NaOH solution are mixed together. What is the strength of the resultant solution? [2018] $\pmb{Sol}~{\rm Given},~N_1$ = 0.1 N, N_2 = 0.2 N, N_3 = 0.5 N and $V_1 = 50 \text{ mL}, V_2 = 100 \text{ mL}, V_3 = 500 \text{ mL}$ Using formula, $N_1V_1 + N_2V_2 + N_3V_3 = N_4V_4$ [Here $V_4 = V_1 + V_2 + V_3 = 50 \text{ mL} + 100 \text{ mL} + 500 \text{ mL}$ = 650 mL] $0.1 \times 50 + 0.2 \times 100 + 0.5 \times 500 = N \times 650$ $5 + 20 + 250 = N \times 650$ $\frac{275}{650} = N$ N = 0.42Strength of a resultant solution = Normality \times equivalent mass $= 0.42 \times 40 = 16.8$ (2)

Important Questions

Q.13 Define and illustrate equivalent mass of an acid.

Sol Equivalent mass of an acid is the ratio of its molecular mass and basicity.

For example, equivalent mass of
$$H_2SO_4$$

= $\frac{\text{Molecular mass of } H_2SO_4}{\text{Basicity}} = \frac{98}{2} = 49 \text{ g}$ (2)

Q.14 What is the molality of a solution containing 40 g of NaOH in 1000 mL of water?

Sol Given,
$$w_B = 40$$

Volume of water = 1000 mL
As we know, molality =
$$\frac{\text{Number of moles of solute}}{\text{Mass of solvent in Kg}}$$

= $\frac{\frac{40}{40}}{1 \text{ kg}} = 1 \text{ molal}$
[: Density of water = 1 g cm⁻¹
and : Mass = Density × Vol.]

(2)

Q.15 A solution obtained by mixing 300 g of 25% and 400 g of 40% solution by mass. Calculate the mass % of the resulting solution.

Sol. 300 g of 25% solution contains solute

$$\frac{300 \times 25}{100} = 75 \,\mathrm{g} \tag{1/2}$$

400 g of 40% solution contains solute $=\frac{400\times40}{100}=160\,\mathrm{g}$

$$\frac{1}{00} = 100 \,\mathrm{g}$$
 (1/2)

Total amount of solute = 160 + 75 = 235 g Total amount of solution = 300 + 400 = 700 g Mass % of solute in resulting solution

$$=\frac{235}{700} \times 100 = 33.5\%$$
 (1/2)

Mass % of water in resulting solution

$$= 100 - 33.5 = 66.5\%$$
 (1/2)

Q.16 How many grams of concentrated nitric acid solution should be used to prepare 250 mL of $2.0 \text{ M} \text{HNO}_3$? The concentrated acid is 70% HNO₃.

Sol. Given, molarity of solution = 2 M

Volume of solution (V) = 250 mL = $\frac{250}{1000}$ L = $\frac{1}{4}$ L

Molar mass of $HNO_3 = 1 + 14 + 3 \times 16 = 63 \text{ g mol}^{-1}$ Molarity = $\frac{\text{Weight of } HNO_3}{\text{Molar mass of } HNO_3 \times V(L)}$

:. Weight of HNO₃ = molarity× molar mass × V (L) = $2 \times 63 \times \frac{1}{4}$ g = 31.5 g (1)

It is the weight of 100% HNO₃. But the given acid is 70% HNO₃.

:. Its weight =
$$31.5 \times \frac{100}{70}$$
 g = 45 g (1)

Q.17 If the molality of an aqueous solution of cane sugar is 0.4445, what is the mole fraction of cane sugar?

Sol. Given that, molality of cane sugar solution

That means, number of moles (n) of cane sugar present in 1 kg of water = 0.4445

We know that, number of moles of water

$$(N) = \frac{1000}{18} = 55.5555$$

Molarity =
$$\frac{1000/18}{1}$$
 = 55.5555 M (1/2)

Mole fraction of cane sugar =
$$\frac{n_{\text{soluce}}}{n_{\text{soluce}} + N_{\text{solvent}}} = \frac{n}{n + N}$$
(1/2)

$$=\frac{0.4445}{0.4445+55.5555}=\frac{0.4445}{56}=0.0079$$
(12)

Q.18 What is the molarity of H_2SO_4 solution which has a density 1.84 g/cc at 35° C and contains 98% by weight?

Sol. 98% by mass means 98 g of
$$H_2SO_4$$
 is present in
100 g of acid.
Molarity, $M = \frac{Mass \text{ of solute} \times 1000}{Molecular \text{ mass} \times \text{Volume}}$ (1/2)

Mass of $H_2SO_4 = 98 \text{ g}$ Molecular mass of $H_2SO_4 = 98 \text{ g} \text{ mol}^{-1}$ Volume of solution $= \frac{\text{Mass}}{\text{Density}} = \frac{100}{1.84}$ (1/2)

Thus, molarity =
$$\frac{98 \times 1000 \times 1.84}{98 \times 100} = 18.4 \text{ M}$$
 (1)

- Q.19 A sample of drinking water was found to be severely contaminated with chloroform (CHCl₃), supposed to be 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.
- Sol. (i) 15 ppm means 15 parts in million or 10^6 parts by mass in the solution.

Therefore, % by mass =
$$\frac{15}{10^6} \times 100 = 15 \times 10^{-4}$$

= 1.5×10^{-3} % (1)

(ii) Taking 15 g chloroform in $10^6\,{\rm g}$ of the solution, mass of solvent $\approx 10^6\,{\rm g}$

Molar mass of
$$CHCl_3 = 12 + 1 + 3 \times 35.5$$

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

$$\therefore \text{ Molality} = \frac{\text{Mass of CHCl}_3 / \text{Molar mass}}{\text{Mass of water (in kg)}}$$

$$= \frac{15 / 119.5}{10^6} \times 1000 = 1.25 \times 10^{-4} \text{ m}$$
(1)

- Q.20 What is the equivalent mass of sodium carbonate? [Textbook]
 - Sol Equivalent mass of sodium carbonate solution $= \frac{\text{Molar mass of Na}_2\text{CO}_3}{\text{Channel}}$

$$=\frac{2 \times 23 + 12 + 3 \times 16}{2} = \frac{106}{2} = 53 \text{ g eq.}$$
(2)

Q.21 Define 'molality'.

29.25 g of NaCl is present in 529.25 g of the solution. Find out the molality. [Textbook] Sol Refer to text on page 20.

- Given, $w_B = 29.25$ g Weight of solution = 599.25 g $\therefore w_B = 529.25 - 29.25$ g = 500 g Molality = Number of moles of solute Mass of solvent in kg = $\frac{29.25}{58} \times 1000$ $= 0.5 \times 2 = 1$ molal (2)
- Q.22 Write down the equation that will show the relationship between normality and molarity. [Textbook]
- Sol Refer to text on page 21.

3 MARK Questions

(2)

Important Questions

- **Q.23** Concentrated nitric acid used in the 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} ?
- Sol. 68% nitric acid by mass means that,

Mass of nitric acid = 68 g

and mass of solution = 100 g

Molar mass of $HNO_3 = 1 + 14 + 3 \times 16 = 63 \text{ g mol}^{-1}$

:. Number of moles of 68 g HNO₃ =
$$\frac{68}{63}$$
 mol = 1.079 mol (1)

: Density of solution =
$$1.504 \text{ g mL}^{-1}$$

: Volume of solution =
$$\frac{100}{1.504}$$
 mL = 66.5 mL = 0.0665 L (1)

Thus, the molarity of the solution

$$= \frac{\text{Moles of the solute}}{\text{Volume of solution (in L)}}$$
$$= \frac{1.079}{0.0665} \text{ M} = 16.23 \text{ M}$$
(1)

- **Q.24** Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol.
- - \therefore 1 mole of benzoic acid = 122 g
 - :. 0.15 mole of benzoic acid = $0.15 \times 122 = 18.3$ g (1)
 - : 0.15 mole are present in 1000 mL of solution.
 - So, 1000 mL of solution contains benzoic acid = 18.3 g
 - $\therefore 250~\mathrm{mL}$ of solution contains benzoic acid

$$=\frac{18.3 \times 250}{1000} = 4.575 \text{ g}$$
(1)

Q.25 Calculate (i) molality (ii) molarity and (iii) mole fraction of KI, if the density of 20% (mass/mass) *aq*. KI is 1.202 g mL^{-1} . Sol. (i) Molality (m) Weight of KI in 100 g of water = 20 g Weight of water in the solution = (100 - 20) g = 80 g = 0.08 kgMolar mass of $KI = 39 + 127 = 166 \text{ g mol}^{-1}$ Molality of the solution $(m) = \frac{\text{Number of moles of KI}}{\text{Mass of water (in kg)}} = \frac{(20 \text{ g})/(166 \text{ g mol}^{-1})}{(0.08 \text{ kg})}$ $= 1.506 \text{ mol kg}^{-1} = 1.506 \text{ m}$ (1) (ii) Molarity (M) Weight of the solution = 100 gDensity of the solution = 1.202 g mL^{-1} Volume of the solution = $\frac{\text{Weight of solution}}{\text{Weight of solution}}$ Density $=\frac{(100 \text{ g})}{(1.202 \text{ g mL}^{-1})} = 83.19 \text{ mL} = 0.083 \text{ L}$ Molarity of the solution (M) $= \frac{\text{Number of gram moles of KI}}{\text{Number of gram moles of KI}}$ Volume of solution in litres $=\frac{(20 \text{ g})/(166 \text{ g mol}^{-1})}{(0.083 \text{ L})} = 1.45 \text{ mol } \text{L}^{-1} = 1.45 \text{ M}$ (1) (iii) Mole fraction of KI

Number of moles of KI,

$$n_{\rm KI} = \frac{\text{Mass of KI}}{\text{Molar mass of KI}} = \frac{20 \text{ g}}{166 \text{ g mol}^{-1}} = 0.12 \text{ mol}$$

Number of moles of water $n_{\rm H_{2}O} = \frac{\rm Mass \ of \ water}{\rm Molar \ mass \ of \ water}$ $= \frac{80 \ g}{18 \ g \ mol^{-1}} = 4.44 \ mol$

Mole fraction of KI

$$\chi_{\rm KI} = \frac{n_{\rm KI}}{n_{\rm KI} + n_{\rm H_2O}} = \frac{(0.12 \text{ mol})}{(0.12 + 4.44) \text{ mol}} = \frac{0.12}{4.56} = 0.0263$$
(1)

- **Q.26** 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 the solution is 1.2 g mL⁻¹, then what shall be the molarity of the solution?
- **Sol.** 10 g glucose is present in 100 g solution, i.e. there is 90 g of water = 0.090 kg of water

Number of moles of 10 g of glucose

$$=\frac{10}{180}$$
 mol= 0.0555 mol

Number of moles of 90 g of
$$H_2O = \frac{90}{18} = 5 \text{ mol}$$

Molality of glucose $=\frac{0.0555 \text{ mol}}{0.090 \text{ kg}}=0.617 \text{ m}$ Mole fraction of glucose, $\chi_{glucose} = \frac{0.0555}{5+0.0555} = 0.01$ (1) $\chi_{(H_2O)} = 1 - 0.01 = 0.99$ (1) Density of solution = 1.2 g mL^{-1} (Given) :. Volume of 100 g solution = $\frac{100}{1.2}$ mL Thus, molarity = $\frac{0.0555 \text{ mol}}{0.08333 \text{ L}}$ = 0.67 M (1) Q.27 Define the term solution. How many types of solutions can be formed? Sol Refer to text on pages 19 and 20. (3) Q.28 Calculate the amount of benzoic acid (C₆H₅COOH) required for preparing 250 mL of 0.15 M solution in methanol. [Textbook] **Sol** Given, Molarity of solution = 0.15 M Volume of solution = 250 mLWe know that. Molarity = $\frac{\text{Number of moles of solute}}{\frac{1}{2}}$ Volume of solution in litres Given mass of solute (w)Molar mass of solute $(M) \times V$ (in L) $\therefore \quad 0.15 = \frac{w \times 1000}{122 \times 250} \implies \frac{0.15 \times 122}{4} = w \implies w = 4.575 \text{ g}$

Thus, amount of benzoic acid required is 4.757 g. (3)

7 MARK Questions

Important Questions

- **Q.29** 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?
 - **Sol.** Suppose, amount of Na_2CO_3 present in the mixture = x g
 - :. NaHCO₃ present in the mixture = (1 x) g Molar mass of Na₂CO₃ = $2 \times 23 + 12 + 3 \times 16$ = 106 g mol⁻¹ Molar mass of NaHCO₃ = $23 + 1 + 12 + 3 \times 16$

$$= 84 \text{ g mol}^{-1}$$

$$\therefore \text{ Moles of } \operatorname{Na}_{2}\operatorname{CO}_{3} \text{ in } xg = \frac{x}{106} \text{ and}$$

moles of NaHCO₃ in $(1 - x)g = \frac{1 - x}{84}$ (2)

As mixture contains equimolar amounts of the two,

$$\therefore \qquad \frac{x}{106} = \frac{1-x}{84} \text{ or } 106 - 106x = 843$$

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

Thus, number of moles of Na $_2 CO_3$ $= \frac{0.558}{106} = 0.00526 \text{ mole}$

and number of moles of NaHCO $_3$ _ 1 – 0.558 _ 0.442

$$\frac{6.000}{84} = \frac{6.112}{84}$$

= 0.00526 mol Again by reaction,

 $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$ $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

 \therefore 1 mole of Na₂CO₃ requires HCl = 2 mol

TOPIC TEST 1

- What is the molality of a solution in which 18 g glucose (mol. wt. = 180g) is dissolved in 500 g of H₂O?
 (a) 0.5 m
 (b) 0.2 m
 (c) 2 m
 (d) 1 m
- 2 The volume of water to be added to 100 cm³ of 0.5 N H₂SO₄ to get decinormal concentration is
 (a) 400 cm³
 (b) 450 cm³
 (c) 500 cm³
 (d) 100 cm³

[Ans. 1.(c), 2.(c)]

- 3 What is the molality of NH_3 in a solution containing 0.85g of NH_3 in 100 mL of a liquid of density 0.85g cm⁻³?
- 4 What is the density of 3.60 M sulphuric acid, which is $29\% H_2SO_4$ by mass?
- 5 A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate
 - (i) mole fraction of sugar.
 - (ii) molality of sugar syrup.
- 6 (i) Calculate the molality of a sulphuric acid solution in which the mole fraction of water is 0.85.
 - (ii) Find the molarity of a solution of CaCl₂, if on chemical analysis, it is found that 200 mL of CaCl₂ solution contains 3.01×10^{22} chloride ions.

= 0.00526 × 2 mol = 0.01052 mol (1) ∴ 1 mole of NaHCO₃ requires HCl = 1 mol ∴ 0.00526 mole of NaHCO₃ requires HCl = 0.00526 mol (1) ∴ Total HCl required = (0.01052 + 0.00526) mol = 0.01578 mol Again, 0.1 mole of 0.1 M HCl is present in 1000 mL of

∴ 0.00526 mole of Na₂CO₃ requires HCl

HCl. $\therefore 0.01578 \text{ mole of } 0.1 \text{ M HCl will be present in HCl}$ $= \frac{1000}{0.1} \times 0.01578 = 157.8 \text{ mL}$ (1)

- 7 What volume of 95% sulphuric acid (density = 1.85 g/cm^3) and what mass of water must be taken to prepare 100 cm³ of 15% solution of sulphuric acid (density = 1.10 g/cm^3)?
- 8 If the density of water of a lake is 1.25 g mL^{-1} and 1 kg of lake water contains 92 g of Na⁺ ions, calcualate the molarity of Na⁺ ions in this lake water. (Atomic mass of Na = 23 g mol^{-1})
- 9 (i) Calculate the molarity of a solution containing $4.9 \text{ g of H}_2\text{SO}_4$ in 500 cm³ of the solution.
 - (ii) A solution contains 25% water, 25% ethanol and 50% acetic acid by mass. Calculate the mole fraction of each component.
- 10 A solution of glucose (molar mass 180 g mol⁻¹) in water is labelled as 10% (by mass). What would be the molality and molarity of the solution?

(Density of the solution = 1.2 g mL^{-1})

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

(1)

(1)

TOPIC~02 Solubility

Solubility of Solute in Solvent

Solubility of a substance is its maximum amount of solute that can be dissolved in a specified amount of solvent (at a specified temperature). It depends on nature of solute, solvent, temperature and pressure, solution can be saturated or unsaturated.

Solubility =
$$\frac{\text{Weight of solute}}{\text{Weight of solvent}} \times 100$$

Saturated Solution

Saturated solution is the solution in which no more solute can be dissolved at the same temperature and pressure.

Unsaturated Solution

An unsaturated solution is the solution in which more solute can be dissolved at the same temperature.

Factors Affecting Solubility

These are given below :

(i) Effect of Temperature

The solubility of a solid in a liquid is significantly affected by temperature change. From Le-Chatelier's principle, if in a nearly saturated solution, the dissolution process is endothermic ($\Delta_{sol}H > 0$), the solubility should increase with rise in temperature and if it is exothermic ($\Delta_{sol}H < 0$), the solubility should decrease. Henry's law is one of the example.

(ii) Effect of Pressure

Pressure does not have any significant effect on solubility of solids in liquids because solids and liquids are highly incompressible and practically remain unaffected by the pressure change.

Solubility of Gases in Liquids

Almost all gases are soluble in water though to different extent. The solubility of any gas in a particular liquid is the volume of the gas (in cubic centimetre, cc) that can be dissolved in unit volume (1cc) of the liquid to form the saturated solution at certain temperature and under a pressure of one atmosphere.

Factors Affecting the Solubility of Gases in Liquids

These are as follows:

(i) **Nature of gas** (solute) **and liquid** (solvent) The solubility of different gases in the same solvent

varies, e.g. gases like hydrogen, oxygen, nitrogen and helium, etc., dissolve in water to a small extent whereas the gases like NH_3 , HCl, SO_2 , etc., are highly soluble in water.

(ii) **Effect of temperature** The solubility of a gas decreases with increase in temperature.

This is because when gas is dissolved in liquid, then on heating the solution containing gas, some gas is usually expelled out of the solution. Also, the dissolution of a gas in a liquid is an exothermic process, so heat is evolved.

So, applying Le-Chatelier's principle, with the increase of temperature, the solubility should decrease. (As gas + solvent \implies solution + heat, equilibrium shifts toward backward direction).

(iii) Effect of pressure The solubility of a gas increases with increase in pressure. In other words, if the gas is compressed over the liquid under high pressure, the solubility increases.

Henry's Law

• It states that, at a constant temperature, the solubility of a gas in liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

$$S \propto p \text{ or } p = K_{\text{H}}.S$$

Unit of solubility is same as concentration.

• The partial pressure of the gas in vapour phase (p) is directly proportional to the mole fraction (χ) of the gas in the solution.

$$p \propto \chi$$
 or $p = K_{\rm H} \cdot \chi$
(where, $K_{\rm H}$ is Henry's law constant)

- If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, we get straight line whose slope is given by $K_{\rm H}.$
- Higher the value of $K_{\rm H}$ at a given pressure, the lower is the solubility of the gas in the liquid. Solubility of gases increases with increase of pressure.

Applications of Henry's Law

- (i) To increase the solubility of CO₂ in soft drinks and soda water, the bottle is sealed under high pressure.
- (ii) To avoid bends and the toxic effects of high concentrations of $\rm N_2$ in the blood, the cylinders used by scuba divers are filled with air diluted with He.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK Questions

Important Questions

- Q.1 Solubility of a gas in liquids depends upon
 (a) nature of the gas (b) temperature
 (c) pressure (d) All of these
- **Sol.** (d) Solubility of a gas in liquids depends upon all the given factors.
- Q.2 Which one of the following gases has the lowest value of Henry's law constant?
 (a) N₂
 (b) He
 (c) CO₂
 (d) O₂
- **Sol.** (c) CO_2 has the lowest value of Henry's law constant.
- **Q.3** The solubility of $N_2(g)$ in water exposed to

the atmosphere, when the partial pressure is 593 mm, is 5.3×10^{-4} M. Its solubility at 760 mm and at the same temperature is (a) 4.1×10^{-4} M (b) 6.8×10^{-4} M (c) 1500 M (d) 2400 M

 $\pmb{Sol.}$ (b) Given, $p_{\rm N_2}$ = 593 mm

when solubility of $N_2 = 5.3 \times 10^{-4}~M$

According to Henry's law,

$$p_{N_2} = K_H \times \chi_{N_2}$$

∴ 593 = $K_H \times 5.3 \times 10^{-4} \text{ M}$
∴ $K_H = \frac{593}{53 \times 10^{-4} \text{ M}} = 111.8 \times 10^4 \text{ bar}$

Therefore, solubility of N₂ at 760 mm can be calculated as $p_{N_2} = K_H \times \chi_{N_2}$

$$\frac{760 \text{ mm}}{111.8 \times 10^4} = \chi_{N_2} \Rightarrow \chi_{N_2} = 6.8 \times 10^{-4} \text{ M}$$

- **Q.4** Why do gases nearly always tend to be less soluble in liquid as the temperature is raised?
- **Sol.** As dissolution of gas in liquid is an exothermic process (Gas + Solvent ⇒ Solution + Heat). So, on increasing the temperature, equilibrium shifts toward the backward direction.
- **Q.5** The $K_{\rm H}$ value for ${\rm H}_2$ in water is 71.18 K bar but its value changes to 3.67 K bar when the solvent is benzene. Why?
- **Sol.** Higher the value of $K_{\rm H}$ for a gas, lower will be its solubility and *vice-versa* Refer to text on page 27.

- **Q.6** Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mm of Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm of Hg.
- **Sol.** According to Henry's law, $p = K_{\rm H} \cdot \chi$

$$\chi = \frac{p}{K_{\rm H}} = \frac{760}{4.27 \times 10^5} = 1.78 \times 10^{-3}$$

So, the mole fraction of methane in benzene is 1.78×10^{-3} .

- Q.7 Explain the solubility rule 'like dissolves like' in terms of intermolecular forces that exist in solutions.
- Sol. Refer to text on page 27.

So

2 MARK Questions

Important Questions

Q.8 Based on solute-solvent interactions, arrange the following in the increasing order of solubility in *n*-octane and explain.

Cyclohexane, KCl, CH₃OH, CH₃CN

- Sol. (i) As cyclohexane and n-octane both are non-polar, hence, they will mix completely in all proportions. (1/2)
 - (ii) KCl is an ionic compound and *n*-octane is non-polar. Hence, KCl will not dissolve in *n*-octane.
 (1/2)
 - (iii) CH_3OH and CH_3CN both are polar but CH_3CN is less polar than CH_3OH . As solvent (*n*-octane) is non-polar, CH_3CN will dissolve more than CH_3OH in *n*-octane. Therefore, the order of solubility will be $KCl < CH_2OH < CH_3CN < cyclohexane$ (1)
- **Q.9** The solubility of $Ba(OH)_2 \cdot 8H_2O$ in water is 5.6 g
 - per 100 g of water at 288 K. Calculate the molality of hydroxide ion in saturated solution of B $a(OH)_2 \cdot 8H_2O$ at that temperature.
- **Sol.** Molar mass of $Ba(OH)_2 \cdot 8H_2O$
 - $= 137 + 2 \times 17 + 8 \times 18 = 315 \text{ g mol}^{-1}$
 - :. 100 g water has 5.6 g of $Ba(OH)_2 \cdot 8H_2O$
 - :. 1000 g water will have Ba(OH)_2 $\cdot 8H_2O$ = 56 g
 - Number of moles of $Ba(OH)_2 \cdot 8H_2O = \frac{56}{315} = 0.178 \text{ mol}$

Thus, molality of
$$Ba(OH)_2 = 0.178 \text{ m}$$
 (1)
 $Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$
Molality of OH^- ions = 2 × molality of $Ba(OH)_2$
= 2× 0.178 = 0.356 m (1)

Q.10 State Henry's law. What is the effect of temperature on the solubility of a gas in a liquid?

- Sol. Henry's law Refer to text on page 27.
 (1)

 Effect of temperature Solubility of gases decreases with increase in temperature.
 (1)
- **Q.11** What is the significance of Henry's law constant $K_{\rm H}$?

Sol. Refer to text on page 27. (2)

3 MARK Questions

Important Questions

- **Q.12** 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
- Sol. (i) Phenol Partially soluble (Reason: Phenol has polar OH group and non-polar C_6H_5 group).
 - (ii) **Toluene** Insoluble (Reason: Toluene is non-polar, water is polar.)
 - (iii) **Formic acid** Highly soluble (Reason: Hydrogen bonding).
 - (iv) **Ethylene glycol** Highly soluble (Reason: Hydrogen bonding).
 - (v) **Chloroform** Insoluble (Reason: H-bonds are formed although polarity is present).
 - (vi) **Pentanol** Partially soluble (Reason: -OHgroup is polar but long hydrocarbon part is non-polar). ($6 \times \frac{1}{2} = 3$)
- **Q.13** 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, respectively. The water is in equilibrium with air at a pressure of 10 atm. At 298 K, if the Henry's law constant for oxygen and nitrogen are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.
- **Sol.** Given that, total pressure of air in equilibrium with water = 10 atm

As air contains 20% oxygen and 79% nitrogen by volume.

$$(p_{O_2}) = \frac{20}{100} \times 10 \text{ arm} = 2 \text{ atm} = 2 \times 760 \text{ mm}$$

= 1520 mm (1/2)

Partial pressure of nitrogen,

$$(p_{N_2}) = \frac{79}{100} \times 10 \text{ atm} = 7.9 \text{ atm} = 7.9 \times 760 \text{ mm}$$

= 6004 mm (1/2)

Given that,
$$K_{\rm H}({\rm O_2})$$
 = 3.30×10^7 mm,
 $K_{\rm H}({\rm N_2})$ = 6.51×10^7 mm

According to Henry's law,

$$p_{O_2} = K_{\rm H} \times \chi_{O_2}$$

or $\chi_{O_2} = \frac{p_{O_2}}{K_{\rm H}} = \frac{1520 \text{ mm}}{3.30 \times 10^7 \text{ mm}} = 4.61 \times 10^{-5}$ (1)

or
$$\chi_{N_2} = \frac{R_H \times \chi_{N_2}}{K_H} = \frac{6004 \text{ mm}}{6.51 \times 10^7 \text{ mm}}$$

= 9.22×10⁻⁵ (1)

- **Q.14** The partial pressure of ethane over a saturated solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution were to contain 5.0×10^{-2} g of ethane, then what will be the partial pressure of the gas?
- **Sol.** According to Henry's law, $m \propto p \implies m = Kp$

$$6.56 \times 10^{-3} \text{ g} = K \times 1 \text{ bar}$$

 $K = 6.56 \times 10^{-3} \text{ g bar}^{-1}$ (1¹/₂)

Again, when
$$m' = 5.00 \times 10^{-2} \text{ g}, p' = ?$$

 $m' = K \times p'$
 $5.00 \times 10^{-2} \text{ g} = 6.56 \times 10^{-3} \text{ g bar}^{-1} \times p'$
 $p' = \frac{5.00 \times 10^{-2}}{6.56 \times 10^{-3}} = 7.62 \text{ bar}$
(1¹/₂)

7 MARK Questions

Important Questions

Q.15 Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

Sol. Step I Calculation of number of moles of CO₂

According to Henry's law,

Mole fraction of $CO_2 (\chi_{CO_2}) = \frac{Partial pressure of <math>CO_2}{K_H \text{ for } CO_2}$ $K_H = 1.67 \times 10^8 \text{ Pa} = \frac{(1 \text{ atm})}{(101325 \text{ Pa})} \times (1.67 \times 10^8 \text{ Pa})$ $= 1.648 \times 10^3 \text{ atm}$ (2)

$$\chi_{\rm CO_2} = \frac{2.5 \text{ atm}}{(1.648 \times 10^3 \text{ atm})} = 1.52 \times 10^{-3}$$
(1)

$$n_{\rm H_2O} = \frac{(500 \text{ g})}{(18 \text{ g mol}^{-1})} = 27.78 \text{ mol}$$
 (1)

$$\chi_{\rm CO_2} = \frac{n_{\rm CO_2}}{n_{\rm CO_2} + n_{\rm H_2O}} = \frac{n_{\rm CO_2}}{n_{\rm H_2O}} = \frac{n_{\rm CO_2}}{(27.78\,{\rm mol})}$$

 $n_{\rm CO_2} = \chi_{\rm CO_2} \times (27.78 \text{ mol})$

TOPIC TEST 2

- 1 The value of Henry's constant ($K_{\rm H}$) is
 - (a) greater for gases with higher solubility
 - (b) greater for gases with lower solubility
 - (c) constant for all gases
 - (d) not related to the solubility of gases
- 2 The mathematical expression for Henry's law is
 - (a) $p = K_{\rm H} \cdot \chi$
 - (c) $p \times K_{\rm H} = \chi$ (d) None of the above

[Ans. 1. (b) 2. (a)]

3 The factors on which solubility depends areand......

[Ans. Temperature and pressure]

(b) $p = \frac{K_{\rm H}}{1}$

- 4 Why do smaller particles dissolve faster than larger ones?
- 5 $\Delta_{sol}H$ of NH₄Cl is > 0. What is the effect of temperature on its solubility?
- 6 Explain, Henry's law about dissolution of a gas in a liquid.

 $= (1.52 \times 10^{-3}) \times (27.78 \text{ mol}) = 0.0422 \text{ mol}$ (1)

Step II Calculation of mass of dissolved CO_2 in water

Mass of CO_2 = Number of moles of $CO_2 \times$

Molar mass of $\rm CO_2$

= $(0.0422 \text{ mol}) \times (44 \text{ g mol}^{-1}) = 1.857 \text{ g}$ (2)

- 7 Consider the solute-solvent interactions and arrange the following compounds in the order of increasing solubility in ethanol with suitable explanations. NaCl, cycloheptane, H₂O, CH₃COCH₃
- 8 Explain, why aquatic species are more comfortable in cold water rather than in hot water?
- **9** $K_{\rm H}$ value for Ar(g), CO₂(g), HCHO(g) and CH₄(g) are 40.39, 1.67, 1.83×10^{-5} and 0.413, respectively. Arrange these gases in the order of their increasing solubility with giving suitable reason.
- 10 What concentration of nitrogen should be present in a glass of water at room temperature? Assume a temperature of 25°C, a total pressure of 1 atm and mole fraction of nitrogen in air is 0.78. $(K_{\rm H} \text{ for nitrogen} = 8.42 \times 10^{-7} \text{ M/mm Hg}).$
- 11 Henry's law constant for CO_2 dissolves in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 1 L of soda water, when packed under 2.5 atm CO_2 pressure at 298 K.

TOPIC~03 Vapour Pressure of Liquid solution, Ideal and Non-ideal Solutions

Vapour Pressure

The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called **vapour pressure**.

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

Raoult's Law

This law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

For component 1, $p_1 \propto \chi_1$ or $p_1 = p_1^{\circ}\chi_1$

Similarly, for component 2, $p_2 = p_2^{\circ} \chi_2$;

According to Dalton's law of partial pressure, the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressure of the components of the solution and is given as:

...

$$p_{\text{total}} - p_1 + p_2$$

$$p_{\text{total}} = p_1^{\circ} \chi_1 + p_2^{\circ} \chi_2;$$

$$p_{\text{total}} = (1 - \chi_2) p_1^{\circ} + \chi_2 p_2^{\circ}$$

$$p_{\text{total}} = p_1^{\circ} + (p_2^{\circ} - p_1^{\circ}) \chi_2 \text{ as } (\chi_1 + \chi_2 = 1)$$

where, p_1° and p_2° are the vapour pressures of pure component 1 and 2 respectively.

If χ_1 and χ_2 are the mole fractions of the component 1 and 2 respectively in vapour phase, then $p_1 = \chi_1 \times p_{\text{total}}$. Similarly, $p_2 = \chi_2 \times p_{\text{total}}$.

Raoult's Law : A Special Case of Henry's Law

In the solution of a gas in a liquid, one of the component is so volatile that it exists as a gas, then we can say that **Raoult's law becomes a special case of Henry's law** in which $K_{\rm H}$ becomes equal to p° .

Ideal and Non-ideal Solutions

If a non-volatile solute is added to a solvent, then the vapour pressure of the solution decreases. This is because in solution, the surface has both solute and solvent molecules, thereby the fraction of the surface covered by the solvent molecules gets reduced, thus reducing the vapour pressure.

On this basis, solution can be classified as ideal or non-ideal.

Ideal Solutions

Ideal solutions obey Raoult's law over entire range of concentration. For these solutions, the enthalpy of mixing $\Delta_{\min} H = 0$ and the volume of mixing $\Delta_{\min} V = 0$. Solutions of *n*-hexane and *n*-heptane, bromoethane and chloroethane, benzene and toluene, etc., are nearly ideal in behaviour.

Non-ideal Solutions

Non-ideal solutions do not obey Raoult's law over entire range of concentration.

For such solutions,

$$\Delta_{\min} H \neq 0 \text{ and } \Delta_{\min} V \neq 0$$

The vapour pressure of non-ideal solution is either higher (positive deviation from Raoult's law) or lower (negative deviation from Raoult's law) than that predicted by Raoult's law.

These are as follows:

Positive Deviation and Negative Deviation

In case of positive deviation from Raoult's law (e.g. mixture of ethanol and acetone, carbon disulphide and acetone), A - B (i.e. solute-solvent) interactions are weaker than those of A - A (solute-solute) or B - B(solvent-solvent) interactions, while in case of negative deviation from Raoult's law (e.g. mixture of phenol and aniline, chloroform and acetone), A - B interactions are stronger than those of A - A or B - B interactions.

The solutions showing **positive deviation** and **negative deviation** from Raoult's law are shown in fig. (a) and (b) respectively.



(i) For positive deviation,

 $\Delta \boldsymbol{H}_{\rm mix} = {\rm Positive}, \, \Delta \boldsymbol{V}_{\rm mix} = \, {\rm Positive}.$

(ii) For negative deviation,

 $\Delta H_{\rm mix} = {\rm Negative}, \Delta V_{\rm mix} = {\rm Negative}.$

Azeotropes

The binary mixtures (solutions) that have the same composition in liquid and vapour phase and boil at constant temperature like a pure liquid are called **azeotropes** or **azeotropic mixtures**. The solutions which show a large negative deviation from Raoult's law, form maximum boiling azeotropes. e.g. nitric acid-water mixture and the solutions which show a large positive deviation from Raoult's law, form minimum boiling azeotropes. e.g. ethanol-water mixture.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

[Textbook]

[Textbook]

1 MARK Questions

Important Questions

- Q.1 When KCl is dissolved in water, the [Textbook] (a) boiling point is raised
 - (b) boiling point is lowered
 - (c) boiling point remains unchanged
 - (d) None of the above
- **Sol** (a) When a non-volatile solute is added into pure solvent, the boiling point is always higher than that of pure solvent.
- Q.2 An aqueous solution of methanol in water has vapour pressure [Textbook]
 - (a) equal to that of water
 - (b) equal to that of methanol
 - (c) more than that of water
 - (d) less than that of water
- **Sol** (c) An aqueous solution of methanol in water has vapour pressure more than that of water. This is due to the formation of stronger solute-solvent interaction through hydrogen bonding.
- Q.3 The vapour pressure of a liquid is equal to the atmospheric pressure at its (boiling point, freezing point). [Textbook]
- Sol boiling point
- Q.4 At 730 mm pressure, the boiling point of water is (more than 100°C, less than 100°C).
- **Sol** less than 100°C
- Q.5 The boiling point of sea water at 760 mm pressure is (more than 100°C, less than 100°C).
- **Sol** more than 100°C
- Q.6 Name one factor which influences the solubility of a solid in a solvent? [Textbook]
- Sol Temperature affects the solubility of a solid in a solvent.

- Q.7 Between water and ether which has a higher vapour pressure? [Textbook]
- *Sol* Between water and ether, ether has higher vapour pressure due to absence of hydrogen bonding.
- Q.8 What is the order of increasing vapour pressure of the following at room temperature? Water, sugar solution in water, alcohol-water solution. [Textbook]
- Sol The order of increasing vapour pressure is : Alcohol - Water solution < Sugar-water solution < Water.
- Q.9 Why is vapour pressure of a solution lower than that of a pure solvent? [Textbook]
- **Sol** In solution, the solvent solute interactions are greater than the solvent solvent interactions in the pure solvent. Hence, the vapour pressure of solution is lower.
- **Q.10** Two liquids *A* and *B* boil at 155°C and 190°C, respectively. Which of them has a higher vapour pressure at 80°C?
- **Sol.** A is more volatile, therefore it has higher vapour pressure.
- **Q.11** How is the vapour pressure of a solvent affected when a non-volatile solute is dissolved in it?
- **Sol.** When a non-volatile solute is added to a solvent, its vapour pressure decreases because some of the surface sites are occupied by solute molecules. Thus, less space is available for the solvent molecule to vaporise.
- **Q.12** Liquids *A* and *B* on mixing produce a warm solution. Which type of deviation from Raoult's law takes place?
- **Sol.** Negative deviation (warm solution means exothermic or greater force of attraction between A and B than A—A or B—B).

- **Q.13** What role does the molecular interaction play in solution of alcohol and water?
- **Sol.** There is strong hydrogen bonding in alcohol molecules as well as water molecules. On mixing these solutions, the molecular interactions are weakened. Hence, they show positive deviations from ideal behaviour. Therefore, the solution will have higher vapour pressure and lower boiling point than that of water and alcohol.

2 MARK Questions

Important Questions

- **Q.14** Describe the effect of temperature on the vapour pressure of a liquid. [Textbook] Sol Refer to text on page 31. (2) Q.15 Define and explain the term "vapour pressure". [Textbook] Sol Refer to text on page 31. (2) Q.16 Define the term 'boiling point'. [Textbook] Sol Refer to text on page 31. (2) Q.17. What is the similarity between Raoult's and Henry's laws? [Textbook] Sol. Both laws are applied to volatile components in solution. (1) Both laws state that "the vapour pressure of one component is proportional to the mole fraction of that component." (1) **Q.18** Heptane and octane form 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 35.0 g of octane?
- **Sol.** Given that, $p_{heptane}^{\circ} = 105.2 \text{ kPa}$,

$$p_{\text{octane}}^{\circ} = 46.8 \text{ kPa}$$

$$\begin{split} & \text{Molar mass of heptane } (C_7 H_{16}) = 100 \text{ g mol}^{-1} \\ & (\text{As } C_7 H_{16} = 7 \times 12 + 16 = 84 + 16 = 100) \\ & \text{Molar mass of octane } (C_8 H_{18}) = 114 \text{ g mol}^{-1} \\ & (\text{As } C_8 H_{18} = 8 \times 12 + 18 = 96 + 18 = 114) \\ & \text{Number of moles of } 26.0 \text{ g heptane} \end{split}$$

$$=\frac{26.0 \text{ g}}{100 \text{ g mol}^{-1}}=0.26 \text{ mol}$$

Number of moles of 35.0 g octane

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

$$\chi_{\text{heptane}} = \frac{0.26 \text{ g}}{0.26 + 0.31} = 0.456$$
(1/2)

$$\chi_{\text{octane}} = 1 - 0.456 = 0.544$$
(1/2)

$$p_{\text{heptane}} = 0.456 \times 105.2 \text{ kPa} = 47.97 \text{ kPa}$$

$$p_{\text{octane}} = 0.544 \times 46.8 \text{ kPa} = 25.46 \text{ kPa}$$

$$p_{\text{total}} = 47.97 + 25.46 = 73.43 \text{ kPa}$$
(1)

- **Q.19** Define an ideal solution and write one of its characteristics.
- Sol. Refer to text on page 31. (2)
- Q.20 What type of deviation is shown by a mixture of ethanol and acetone? Give reason.
- Sol. A mixture of ethanol and acetone shows positive deviation because in this case, A B interactions are weaker than A A and B B interactions. Due to this, vapour pressure increases which results in positive deviation. (1+1)
- **Q.21** Explain, why a solution of chloroform and acetone shows negative deviation from Raoult's law?
- Sol. Refer to text on page 31. (2)
- **Q.22** What is meant by the positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for positive deviation ?
- Sol. Refer to text on page 31. (2)
- Q.23 Vapour pressure of water is 1.23 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it. [Textbook]
- **Sol** As solution is 1 molal, it means that 1 mole of solute is dissolved in 1000 g of solvent (water).

No. of moles of solute = 1 mol,
$$p_{\text{solvent}}^{\circ}$$
 = 12.3 kPa
No. of moles of water = $\frac{1000}{18}$ = 55.55 mol

Total moles = 56.55 mol

Mole fraction of water =
$$\frac{\chi_1(\text{solvent})}{\chi_1 + \chi_2(\text{solution})} = \frac{55.55}{56.55}$$
 (1)

$$p_{\text{solution}} = p_{\text{solvent}}^{\circ} \times \chi_{\text{H}_{2}\text{O}}$$

$$p_{\text{solution}} = 12.3 \times \frac{55.55}{56.55} = 12.08 \text{ kPa}$$
(1)

Q.24 Benzene and toluene both have equal mole fractions in their mutual solution. What do you expect about their mole fraction in vapour phase at the same temperature?

(Given,
$$p^{\circ}_{\text{benzene}} = 3p^{\circ}_{\text{toluene}}$$
)

Sol. :: $\chi_{\rm B} = \chi_{\rm T}$ (mole fractions are equal)

$$\frac{p_{\rm B}}{p_{\rm T}} = \frac{p_{\rm B}^{\circ}}{p_{\rm T}^{\circ}} \tag{1}$$

But given that, $\frac{p_B^{\circ}}{p_T^{\circ}} = 3$ $\therefore \frac{p_B}{p_T} = 3$

B

ut
$$\frac{p_{\rm B}}{p_{\rm T}} = 3$$
 shows that $\frac{y_{\rm B}}{y_{\rm T}} = 3$ in vapour phase, since

vapour pressures in vapour phase are in the ratio of their number of moles or mole fractions. (1)

7 MARK Questions

Exams' Questions

- Q.25 State Raoult's law. How is the molecular mass of a solute determined from lowering of vapour pressure measurement? [2019]
- Sol Raoult's Law The French Chemist, Francois Marte Raoult gave a quantitative relationship between the partial pressures and the mole fractions of two components. This relationship is known as Raoult's law, which states that, "At a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution".

Let two volatile liquids 1 and 2 have mole fractions as x_1 and x_2 , respectively. If p_1 and p_2 are vapour pressures of these components in the solution, then according to Raoult's law

For component 1, $p_1 \propto x_1$ and $p_1 = p_1^{\circ} x_1$

Similarly, for component 2, $p_2 = p_2^{\circ} x_2$

where, p_1° is the vapour pressure of pure component

1 and $p_2^{\rm o}$ is the vapour pressure of pure component 2 at same temperature. (1)

Determination of Molecular Mass of Solute

Let, x_1 is the mole fraction of solvent, x_2 is that of solute, p_1° is the vapour pressure of pure solvent and *p* is that of solution.

According to Raoult's law, $p_1 = p_1^{\circ} x_1$ or $p = p_1 = p_1^{\circ} x_1$ Since, x_1 is always less than 1, so vapour pressure of the solution will always be less than the vapour pressure of pure solvent (p_1°) .

So, lowering in vapour pressure of solvent is

$$\begin{split} \Delta p_1 &= p_1^\circ - p_1 = p_1^\circ - p_1^\circ x_1 = p_1^\circ (1-x_1) \\ \text{But}, \qquad \qquad x_1 = 1-x_2 \text{ or } x_2 = 1-x_1 \end{split}$$

 $\Delta p_1 = p_1^{\circ} x_2$ or $x_2 = \frac{\Delta p_1}{1} = \frac{p_1^{\circ} - p_1}{1}$ So,

So, relative lowering in vapour pressure of an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temperature.

Let, W_1, W_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute, respectively. If n_2 moles of solute be dissolved in n_1 moles of the solvent, then the mole fraction if the solute = $\frac{n_2}{n_2}$

For very dilute solutions, $n_2 \ll n_1$

$$x_2 = \frac{W_2/M_2}{W_1/M_1}$$

So, $\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \frac{W_2M_1}{W_1M_2}$ or $\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \frac{n_2}{n_1}$

Thus, molar mass of solute can be determined by

$$M_{2} = \frac{W_{2}M_{1}}{W_{1}\left(\frac{p_{1}^{\circ} - p_{1}}{p_{1}^{\circ}}\right)}$$
(2)

Important Questions

- Q.26 At 25°C, the vapour pressures of benzene (C_6H_6) and toluene (C_7H_8) are 93.4 torr and 26.9 torr, respectively. A solution is made by mixing 35.0 g of benzene and 65.0 g of toluene. At what applied pressure, in torr, will this solution boil at 25° C?
- Sol. This solution of benzene and toluene will boil at 25° C when the pressure above the solution is equal to the sum of the vapour pressures of benzene and toluene in the solution. Partial vapou

 $p^\circ_{\rm C_6H_6}=93.4$ torr

Partial vapour pressure of toluene,

$$p^{\circ}_{C_{6}H_{5}CH_{3}} = 26.9 \text{ torr}$$

Mass of $C_6H_6 = 35$ g and mass of $C_6H_5CH_3 = 65$ g Molar mass of $C_6H_6 = 12 \times 6 + 1 \times 6$

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

Therefore, the number of moles of C_6H_6 ,

$$n_{\rm C_6H_6} = \frac{35}{78} = 0.449 \tag{1/2}$$

Molar mass of $C_6H_5CH_3 = 12 \times 6 + 1 \times 5 + 12 + 1 \times 3$ $= 92 \text{ g mol}^{-1}$

Therefore, the number of moles of
$$C_6H_5CH_3$$
,

$$n_{\rm C_6H_5CH_3} = \frac{65}{92} = 0.707 \tag{1/2}$$

Now, the mole fractions of C_6H_6 and $C_6H_5CH_3$ are

$$\chi_{C_6H_6} = \frac{n_{C_6H_6}}{n_{C_6H_6} + n_{C_6H_5CH_3}}$$
$$= \frac{0.449}{0.449 + 0.707} = \frac{0.449}{1.156} = 0.388$$
 (1/2)

$$\chi_{C_6H_5CH_3} = \frac{n_{C_6H_5CH_3}}{n_{C_6H_5CH_3} + n_{C_6H_6}}$$
$$= \frac{0.707}{0.707 + 0.449} = \frac{0.707}{1.156} = 0.612$$
 (1/2)

Therefore, vapour pressure of C₆H₆ and C₆H₅CH₃ are

$$p_{C_6H_6} = p_{C_6H_6}^{\circ} \times \chi_{C_6H_6}$$

= 93.4 × 0.388 = 36.24 torr

$$p_{C_{6}H_{5}CH_{3}} = p_{C_{6}H_{5}CH_{3}}^{\circ} \times \chi_{C_{6}H_{5}CH_{3}}$$

= 26.9 × 0.612 = 16.46 torr

Total vapour pressure of the solution,

$$p_{\text{total}} = p_{C_6H_6} + p_{C_6H_5CH_3}$$

= 36.24 +16.46 = 52.7 torr (1)

- **Q.27** 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.
- Sol. Number of moles of liquid A (solute) $= \frac{100 \text{ g}}{140 \text{ g mol}^{-1}} = \frac{5}{7} \text{ mol}$ Number of moles of liquid $B = \frac{1000 \text{ g}}{180 \text{ g mol}^{-1}} = \frac{50}{9} \text{ mol}$ ∴ Mole fraction of A in the solution (χ_A) $= \frac{5/7}{5/7 + 50/9} = \frac{5/7}{395/63}$ $= \frac{5}{7} \times \frac{63}{395} = \frac{45}{395} = 0.114$ (1/2)

:. Mole fraction of B in the solution (χ_B) = 1-0.114=0.886 (1/2)

Also, given $p_B^\circ = 500$ torr

According to Raoult's law,

or

or

$$p_{A} = \chi_{A} p_{A}^{\circ} = 0.114 \times p_{A}^{\circ} \qquad \dots (i)$$

$$p_{B} = \chi_{B} p_{B}^{\circ} = 0.886 \times 500 = 443 \text{ torr}$$

$$p_{\text{total}} = p_{A} + p_{B}$$

$$475 = 0.114 p_{A}^{\circ} + 443$$

$$p_{A}^{\circ} = \frac{475 - 443}{0.114} = 280.7 \text{ torr} \qquad (1)$$

Substituting the value of p_A° in Eq. (i), we get

$$p_A = 0.114 \times 280.7 \text{ torr } = 32 \text{ torr}$$
 (1)

Q.28 Vapour pressure of pure acetone and chloroform at 328 K are 741.8 mm of Hg and 632.8 mm of 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 χ_{acetone} . The experimental data observed for different compositions of mixture is

$100 imes \chi_{acetone}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{\rm acetone}/{ m mm}$ of Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{ m chloroform}/ m mm$ of 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.

Sol.

Xacetone	0.0	0.118	0.234	0.360	0.508	0.582	0.645	0.721
$p_{\rm acetone}/{ m mm}$ of Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\rm chloroform}/{ m mm}$ of Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7
p_{total}	632.8	603.1	579.7	562.4	580.9	600.0	615.9	642.5



As the plot for p_{total} dips downwards, hence the solution shows negative deviation from Raoult's law.

(4)

TOPIC TEST 3

- A solution containing components A and B follows Raoult's law, when
 - (a) A-B attraction force is greater than A-A and B-B
 - (b) A-B attraction force is less than A-A and B-B
 - (c) *A-B* attraction force remains same as *A-A* and *B-B*
 - (d) volume of solution is different from sum of volumes of solute and solvent
- **2.** Which of the following will show a negative deviation from Raoult's law?
 - (a) Acetone-benzene (b) Acetone-ethanol
 - (c) Benzene-methanol (d) Acetone-chloroform
- **3.** Which of the following azeotropic solutions has the boiling point less than boiling point of the constituents *A* and *B* ?
 - (a) CHCl₃ and CH₃COCH₃
 (b) CS₂ and CH₃COCH₃
 (c) CH₃CH₂OH and CH₃COCH₃
 (d) CH₃CHO and CS₂
- **4.** The solution which shows large positive deviation from Raoult's law form
 - (a) maximum boiling azeotrope at a specific composition
 - (b) maximum freezing azeotrope at a specific composition
 - (c) minimum boiling azeotrope at a specific composition
 - (d) minimum freezing azeotrope at a specific composition [Ans. 1. (c), 2. (d), 3. (a), 4. (c)]
- 5. How much urea should be dissolved in 50 g of water so that its vapour pressure at room temperature is reduced by 25%.

- **6.** The vapour pressure of pure liquids A and B are 450 and 700 mm of Hg respectively at 350 K. Find out the composition of the liquid mixture, if total vapour pressure is 600 mm of Hg. Also, find the composition of the vapour phase.
- 7. Defined azeotropes? What type of azeotropes is formed by negative deviation from Raoult's law? Give an example.
- **8.** At a given temperature, the vapour pressure in mm of Hg of a solution of two volatile liquids *A* and *B* is given by the equation.

 $p = 120 - 80 \times \chi_B$ [where, $\chi_B =$ mole fraction of *B*] Calculate the vapour pressure of pure *A* and *B* at the same temperature.

- **9.** At 298 K, the vapour pressure of pure liquid, *n*-butane is 1823 torr and vapour pressure of pure liquid, *n*-pentane is 521 torr form nearly an ideal solution.
 - (i) Find the total vapour pressure at 298 K of a liquid solution containing 10% *n*-butane and 90% *n*-pentane by weight.
 - (ii) Find the mole fraction of *n*-butane in solution exerting a total vapour pressure of 760 torr.
 - (iii) What is the composition of vapours of two components (mole fraction in vapour state)?
- **10.** What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{mix}H$ related to positive and negative deviations from Raoult's law?

TOPIC ~04 Colligative Properties and Determination of Molecular Mass

Colligative Properties

The properties of solutions which depend only on the number of solute particles, irrespective of their nature relative to the total number of particles present in solution are known as colligative properties.

There are four important colligative properties which are discussed below :

Relative Lowering of Vapour Pressure

When a non-volatile solute is dissolved in a solvent, vapour pressure of the solution becomes lower than that of the pure solvent which is known as **lowering of vapour pressure**. The relative lowering of vapour pressure of a solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temperature. The expression for relative lowering of vapour pressure (**Raoult's law for non-volatile solute**) can be written as:

$$\frac{\Delta p_1}{p_1^{\circ}} = \frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \chi_2$$

Here, $\Delta p_1 =$ lowering in vapour pressure of solvent $p_1^{\circ} =$ vapour pressure of pure solvent

 $P_1 =$ vapour pressure of solution

$$\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \frac{n_2}{n_1 + n_2} \qquad \left(\text{Since, } \chi_2 = \frac{n_2}{n_1 + n_2}\right)$$
$$\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \frac{n_2}{n_1} \text{ (For dilute solutions, } n_2 << n_1\text{)}$$

$$\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

Here, W_1, W_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute, respectively.

or

$$M_2 \text{ (solute)} = \frac{W_2 M_1}{W_1 \left(\frac{p_1^\circ - p_1}{p_1^\circ}\right)}$$

Elevation in Boiling Point

The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure. The boiling point of a solution containing a non-volatile solute is always less than the freezing point of the pure solvent. This increase in boiling point is termed as **elevation in boiling point**.

If T_b° is boiling point of pure solvent and T_b is the boiling point of solution, then the elevation in boiling point (ΔT_b) is represented as,

$$\Delta T_b = T_b - T_b^\circ$$

Elevation in boiling point,

$$\Delta T_b \propto m$$
 (where, *m* is molality)

or
$$\Delta T_b = K_b m$$
 or $\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1 \text{ (g)}}$

Also,
$$K_b = \frac{R \times M_1 \times (T_b^\circ)^2}{1000 \times \Delta_{\text{vap}} H}$$
 or $M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1(g)}$

(where, K_b = boiling point elevation constant or molal elevation constant or ebullioscopic constant having unit K kg mol⁻¹)

Depression in Freezing Point

The freezing point of a substance is that temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in solid phase. When a non-volatile solute is added to a solvent, the freezing point of the solution is always lower than that of pure solvent as the vapour pressure of the solvent decreases in the presence of non-volatile solute. This difference in freezing point is known as depression of freezing point, i.e. $\Delta T_f = T_f^{\circ} - T_f$. where, T_f° is the freezing point of pure solvent and T_f is the freezing point of solution. Then, depression of freezing point,

$$\begin{split} \Delta T_f & \propto m ~~ \text{or} ~ \Delta T_f = K_f m \\ \Delta T_f & = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1 ~(\text{g})} \end{split}$$

where, K_f = freezing point depression constant or molal depression constant or cryoscopic constant, having unit K kg mol⁻¹

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1(g)}$$

Also,
$$K_f = \frac{R \times M_1 \times (T_f^\circ)^2}{1000 \times \Delta_{\text{fus}} H}$$

where, R and M_1 are gas constant and molar mass of the solvent, respectively. T_f° and T_b° are freezing and boiling point of the pure solvent, respectively (in K). $\Delta_{\text{fus}}H$ and $\Delta_{\text{vap}}H$ are enthalpies for the fusion and vaporisation of the solvent, respectively.

Osmosis and Osmotic Pressure

The process of flow of solvent molecules from solution of lower concentration to solution of higher concentration through semipermeable membrane is known as osmosis. The hydrostatic pressure which develops on account of osmosis is called **osmotic pressure** or the excess pressure that must be applied on the solution to prevent osmosis is called **osmotic pressure**.

Osmotic pressure (π) is directly proportional to molarity (C) of the solution at a given temperature (T).

$$\pi = CRT$$
 or $\pi = \frac{n_2}{V}RT$ (where, $C = \frac{n_2}{V}$)

where, n_2 is the number of moles of solute dissolved in VL of solution, W_2 is the weight of solute and M_2 is the molar mass of solute.

or
$$\pi V = \frac{W_2 RT}{M_2}$$
 or $M_2 = \frac{W_2 RT}{\pi V}$

- -- C

Osmotic pressure is used to determine molar masses of proteins, polymers and other macromolecules.

- (i) Two solutions having same osmotic pressure at a given temperature are called **isotonic solutions**.
- (ii) A solution having lower osmotic pressure than the other solution is called **hypotonic** while, the one with higher osmotic pressure is called **hypertonic**.
- (iii) **Reverse osmosis** If a pressure larger than the osmotic pressure is applied to the solution side, then the pure solvent flows out of the solution through the semipermeable membrane. This phenomenon is called **reverse osmosis**. It is used for the desalination of sea water.

Abnormal Molar Mass

For the substances undergoing association, dissociation, etc. in the solution, molecular mass determined from colligative properties is different from the expected value. This is known as abnormal molar mass.

van't Hoff Factor

It is the ratio of the experimental value of colligative property to the calculated value of the colligative property. It is used to find out the extent of dissociation or association.

van't Hoff factor

i = <u>Normal molar mass</u> Abnormal molar mass Total number of moles of particles after = <u>association / dissociation</u>

Number of moles of particles before association /dissociation

 $= \frac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$

If i>1 , solute undergoes dissociation, and if i<1 ,

solute undergoes association.

• For association, when molecules of solute forms dimer, n = 2.

Degree of association, $\alpha = \frac{i-1}{\left(\frac{1}{n}-1\right)}$

where, n = number of particles associated.

• For dissociation of the solute AB type, m = 2, and for the solute AB_2 or A_2B type (CaCl₂, Na₂SO₄), m = 3. Degree of dissociation,

$$\alpha = \frac{\iota - 1}{m - 1}$$

where, m = number of particles dissociated.

- Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:
 - (i) Relative lowering of vapour pressure of solvent,

$$\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = i \frac{n_2}{n_1}$$

- (*ii*) Elevation in boiling point, $\Delta T_b = i K_b m$
- (*iii*) Depression in freezing point, $\Delta T_f = i K_f m$
- (iv) Osmotic pressure of solution,

$$\pi = \frac{in_2}{V} RT$$

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK Questions

Exams' Questions

- Q.1 When the value of van't Hoff factor is less than one, this shows that the solute undergoes ______ in the solution. [2019]
- **Sol** If value of van't Hoff factor is less than one, this shows that the solute undergoes **association** in the solution.

Number of solute particles after association /dissociation in the solution

Since, $i = \frac{\text{Aussociation in the solution}}{\text{Number of solute particles originally taken}}$ in the solution

Thus, if i = 1, (No association/dissociation) If, i < 1 (Show association) and if, i > 1 (Show dissociation)

Important Questions

- **Q.2** Explain boiling point elevation constant for a solvent.
- Or Define molal elevation constant, K_{h} .
- **Sol.** We know that, $\Delta T_b = K_b m$

If m = 1, then $\Delta T_b = K_b$. Thus, boiling point elevation constant is equal to the elevation in boiling point,

when 1 mole of a solute is dissolved in 1 kg of solvent. It is also called ebullioscopic constant.

- **Q.3** Out of 0.1 molal solutions of glucose and sodium chloride each, will have a higher boiling point.
- **Sol.** 0.1 molal solution of NaCl (because it dissociates into its ions in solution, i.e. it has more number of ions.)
- **Q.4** Will the depression in freezing point be same or different, if 0.1 mole of sugar or 0.1 mole of glucose is dissolved in 1 L of water?
- **Sol.** It will be same for both solutions because both are non-electrolytes and give same number of solute particles.
- Q.5 What is de-icing agent? How does it function?
- **Sol.** Common salt acts as de-icing agent because it lowers the freezing point of water to such an extent that it does not freeze to form ice. It is used to clear snow from roads.
- Q.6 When a dry grape or raisin is placed in water, it swells due to [Textbook] (a) diffusion
 - (b) osmosis
 - (c) absorption
 - (d) surface tension

- **Sol** (b) When a dry grape or raisin is placed in water, it swells due to osmosis. It is the phenomenon of spontaneous flow of solvent molecules through a semipermeable membrane molecules from pure solvent to the solution.
- Q.7 What is the relationship between depression in freezing point of a solution and molecular mass of the solute? [Textbook]
- Sol The relationship between depression in freezing point of a solution and molecular mass of the solute is given as follows :

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

Q.8 What is reverse osmosis and how is it helpful? [Textbook]

Sol Refer to text on page 37.

Q.9 What do you understand by "osmotic pressure". [Textbook]

Sol Refer to text on page 37.

2 MARK Questions

Important Questions

- Q.10 Calculate the vapour pressure of the solution at 100°C containing 3 g of cane sugar in 33 g of water. [molecular weight of sugar = 342] [Textbook]
- Sol Vapour pressure of pure water (solvent) at 100°C, $p^{\circ} = 760 \text{ mm}.$ Vapour pressure of solution, p = ?Weight of solvent, W = 33 g Weight of solute, w = 3 g Molecular weight of water (H₂O), M = 18Molecular weight of sugar (C₁₂H₂₂O₁₁) $m = 12 \times 12 + 22 \times 1 + 11 \times 16 = 342$

According to Raoult's law,

$$\frac{p^{\circ} - p}{p^{\circ}} = \frac{wM}{Wm} \Longrightarrow p = p^{\circ} - \frac{w \times M}{m \times W} \times p^{\circ}$$
$$p = 760 - \frac{3 \times 18}{342 \times 33} \times 760$$

[:: p° for H₂ = 760 mm] p = 760 - 3.19 = 756.90 mm(2)

Q.11 Distinguish between diffusion and osmosis.

Diffusion	Osmosis
It is movement of solute particle.	It is movement of solvent particle.
No membrane is required.	Semi-permeable membrane is required.
Movement occurs from high concentration to low concentration.	Movement occurs from low concentration to high concentration.
It is found in both liquids and gases.	It is found only in liquids.

Q.12 18 g of glucose, $C_6H_{12}O_6$ (molar mass = 180 g mol⁻¹) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil? $(K_b \text{ for water} = 0.52 \text{ K kg mol}^{-1}, \text{ boiling point of})$ pure water = 373.15 K).

$$\begin{split} W_{a} &= \text{weight of } H_{2}\text{O} \text{ (solvent)} = 1 \text{ kg} \\ W_{b} &= \text{weight of } C_{6}\text{H}_{12}\text{O}_{6} \text{ (glucose, solute)} = 18 \text{ g} \\ T_{b}^{\circ} &= 373.15 \text{ K} \\ K_{b} &= 0.52 \text{ K kg mol}^{-1} \\ M_{b} &= \text{molar mass of solute (glucose)} = 180 \text{ g mol}^{-1} \\ \Delta T_{b} &= \frac{K_{b} \times 1000 \times W_{b}}{M_{b} \times W_{a}} = \frac{(0.52 \text{ K kg mol}^{-1}) \times 1000 \times 18 \text{ g}}{(180 \text{ g mol}^{-1}) \times 1000 \text{ g}} \\ &= \frac{9360}{180000} = 0.052 \text{ K} \end{split}$$
(1)

As we know that,

$$\Delta T_b = T_b - T_b^{\circ}$$

$$0.052 = T_b - 373.15$$

$$T_b = 373.15 + 0.052 = 373.202 \text{ K}$$

$$\approx 373.20 \text{ K (approx.)}$$
(1)

- Q.13 Explain, why on addition of 1 mole of NaCl to 1 L of water, the boiling point of water increases, while addition of 1 mole of methyl alcohol to 1 L of water decreases its boiling point?
- Sol. NaCl is a non-volatile solute. So, its addition to water lowers the vapour pressure of water. Hence, boiling point of water (solution) increases. Whereas, methyl alcohol is more volatile than water. So, its addition to water increases the total vapour pressure of the solution. It results in decrease of boiling point of water. (2)
- Q.14 Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g of octane to reduce its vapour pressure to 80%.
- **Sol.** Here, p = 80% of $p_1^\circ = 0.80 p_1^\circ$

Number of moles of solute
$$(n_2) = \frac{W_2}{40}$$
 mol

Number of moles of solvent (octane)

$$(n_1) = \frac{114 \text{ g}}{114 \text{ g mol}^{-1}} = 1 \text{ mol}$$

(: As molar mass of $C_8H_{18} = 114 \text{ g mol}^{-1}$)

Now,

$$\frac{p_1^{\circ} - p}{p_1^{\circ}} = \chi_2 = \frac{n_2}{(n_1 + n_2)}$$
(1)

$$\therefore \qquad \frac{p_1^{\circ} - 0.80 p_1^{\circ}}{p_1^{\circ}} = \frac{(W_2/40)}{(W_2/40 + 1)}$$
(1)

$$0.2 \left(\frac{W_2}{40} + 1\right) = \frac{W_2}{40} \text{ or } \frac{0.8W_2}{40} = 0.2$$
or

$$W_2 = 10 \text{ g}$$
(1)

(2)

3 MARK Questions

Exams' Questions

or

- Q.15 The osmotic pressure of a solution containing 50 g of a solute in one litre of solution at 300 K is 20.5 atmosphere. Calculate the molecular mass of the solute. [2019]
- **Sol** Given, osmotic pressure $(\pi) = 20.5$ atm

Volume of solution (V) = 1 L Mass of solute $(w_B) = 50$ g Temperature (T) = 300 K Gas constant (R) = 0.082 L atm K⁻¹ mol⁻¹ To find, molar mass of solute $(M_B) = ?$ Relation used :

$$\pi = CRT \Rightarrow \pi = \frac{w_B \times KI}{M_B \times V}$$
$$\pi = \frac{50 \times 0.082 \times 300}{M_B \times 1}$$
$$M_B = \frac{50 \times 0.082 \times 300 \times 1}{20.5}$$
$$M_B = 60.00$$

Thus, molecular mass of solute = 60.00 g/mol

Q.16 Boiling point of water is 100°C. Calculate the boiling point of an aqueous solution containing 5g urea (Mol. mass = 60) in 100 g water (K_b for water = 0.52 K kg mol⁻¹). [2018]

 $\begin{array}{l} \textit{Sol} \ \mbox{Given, boiling point of water} = 100^{\circ} \ \mbox{C} \\ (273 + 100 = 373 \ \mbox{K}) \\ \mbox{Weight of water} \ (W_1) = 100 \ \mbox{g} = 0.1 \ \mbox{kg} \\ \mbox{Molal elevation constant} \ (K_b) = 0.52 \ \mbox{K Kg mol}^{-1} \\ \mbox{Weight of solute (urea)} \ (W_2) = 5 \ \mbox{g} \\ \mbox{Molar mass of urea} = 60 \ \mbox{g mol}^{-1} \\ \mbox{We know that, } \Delta T_b = K_b m \\ T_b - T_b^{\circ} = \frac{K_b \times W_2}{M_2 \times W_1} \\ T_b - 373 \ \mbox{K} = \frac{0.52 \ \mbox{K Kg mol}^{-1} \times 5 \ \mbox{g}}{60 \ \mbox{g mol}^{-1} \times 0.1 \ \mbox{kg}} \end{array}$

$$= 373.4 \text{ K or } 100.4^{\circ}\text{C}$$
 (3)

Important Questions

- Q.17 A solution of sucrose is prepared by dissolving 68.4 g in 1000 g of water. Calculate the vapour pressure of solution at 20°C. The vapour pressure of water of 298 K is 0.023 atm. Assume that the solution behaves ideally.
 (Molar mass of sucrose = 342 g mol⁻¹). [Textbook]
- **Sol** Given, $W_B = 68.4$ g
 - :. Number of moles of sucrose = $\frac{68.4}{342}$

 T_b

$$W_A = 1000 \text{ g}$$

∴ Number of moles of water $= \frac{1000}{18}$

According to lowering of vapour pressure,

 $\frac{p^{\circ} - p}{p^{\circ}} = \chi_2$

÷.

(3)

where, p° = vapour pressure of pure water = 0.023 atm p = vapour pressure of solution = ?

$$\frac{0.023 - p}{0.023} = \frac{\frac{68.4}{342}}{\frac{68.4}{342} + \frac{1000}{18}}$$
$$\frac{0.023 - p}{0.023} = 0.00359$$
$$0.023 - p = 0.00008257 \implies p = 0.02292 \text{ atm. (3)}$$

- **Q.18** A solution containing 18 g of non-volatile solute in 200 g of water freezes at 272.07 K. Calculate the molecular mass of the water (Water freezes at 273 K and its $K_f = 1.800 \text{ kg mol}^{-1}$). [Textbook]
- Sol Given, Mass of solute = 18 g Mass of solvent = 200 g Initial temperature = 272.07 K Freezing point of water = 273.15 Formula used: $\Delta T_f = K_f \times m$ where, *m* is molality

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

$$\Delta T_f = K_f \times \frac{w_{\text{solute}}}{M_{\text{solute}} \times w_{\text{solvent}}}$$

$$\therefore \qquad M_{\text{solute}} = \frac{(1.86 \text{ K kg/mol}) \times 18 \text{ g}}{(200 \text{ g}) (273.15 \text{ K} - 272.07 \text{ K})}$$

= 0.155 kg/mole = 155 g/mol

Therefore, the molar mass of the solute 155 g/mol. (3)

- **Q.19** The boiling point of a solution containing 5.0 g of non-volatile solute in 1 kg of a solvent at 0.05° higher than that of pure solvent. Calculate the molecular mass of the solute (Molecular mass and K_b for a solvent are 78 and 2.53 K kg/mol⁻¹ respectively). [Textbook]
- **Sol** Given, $w_{\text{solute}} = 5.0 \text{ g}$

$$w_{\text{solvent}} = 1 \text{ kg}$$

 $\Delta T_{h} = 0.05^{\circ}$

According to elevation in boiling point, we have

$$M_{\text{solute}} = \frac{K_b \times w_{\text{solute}}}{\Delta T_b \times W_{\text{solvent}} \text{ (in kg)}}$$
$$= \frac{2.53 \text{ K kg/mol} \times 5.0 \text{ g}}{0.05 \times 1 \text{ kg}}$$
$$= 253 \text{ g mol}^{-1}$$

Thus, molecular mass of the solute is 253 g mol^{-1} .(3)

- Q.20 A solution of 2.4 g of a substance in 25 g water boiled at 100.8°C at 1 atm pressure. Calculate the molecular mass of the substance (Boiling elevation constant for water = 0.52°C per 1000 g of it). [Textbook]
 - **Sol** Given, $w_{\text{solute}} = 2.4 \text{ g}$

 $w_{\text{solvent}} = 25 \text{ g}$ $T_b = 100.8^{\circ}\text{C}$ $\therefore \qquad \Delta T_b = T_b - T_b^{\circ} = 100.8^{\circ} - 100^{\circ} = 0.8^{\circ}\text{C}$ According to elevation in boiling point, $M_{\text{solute}} = \frac{K_b \times w_{\text{solute}} \times 1000}{\Delta T_b \times w_{\text{solvent}}} \text{ (g)}$

$$= \frac{0.52 \times 2.4 \times 1000}{0.8^{\circ} \text{C} \times 25 \text{ g}}$$

 \therefore $M_{\text{solute}} = 77.8 \text{ or } 78 \text{ g mol}^{-1}$

Thus, molecular mass of substance is 78 g mol^{-1} . (3)

Q.21 At 25°C, the saturated vapour pressure of water is 3.165 kPa (23.75 mm of Hg). Find the saturated vapour pressure of a 5% aqueous solution of urea (carbamide) at the same temperature. (Molar mass of urea = 60.05 g mol⁻¹).

Sol.
$$\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \chi_2 = \frac{n_2}{n_1}$$
 [for dilute solution, $n_2 << n_1$]

 $p_1^\circ = 3.165 \text{ kPa},$

$$\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

(1)

Given,

$$\begin{split} W_2 &= 5 \text{ g}, W_1 = 95 \text{ g} \\ M_2 &= 60.05 \text{ g mol}^{-1}, \\ M_1 &= 18 \text{ g mol}^{-1} \\ \frac{3.165 - p_1}{3.165} &= \frac{5 \times 18}{60.05 \times 95} \Rightarrow 0.0158 \end{split} \tag{1}$$

$$3.165 - p_1 = 0.050$$
 or $p_1 = 3.115$ kPa (1)

- **Q.22** Vapour pressure of pure water at 298 K is 23.8 mm of Hg. 50 g of urea (NH_2CONH_2) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.
- **Sol.** Given, $p^{\circ} = 23.8 \text{ mm of Hg}$, $W_2 = 50 \text{ g}$, $W_1 = 850 \text{ g}$ For solute, urea (NH₂CONH₂), $M_2 = 60 \text{ g mol}^{-1}$ For solvent (H₂O), $M_1 = 18 \text{ g mol}^{-1}$ According to Raoult's law,

$$\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \frac{n_2}{n_1 + n_2} \text{ or } \frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \frac{n_2}{n_1} = \frac{W_2 / M_2}{W_1 / M_1}$$
(For dilute solution, $n_1 + n_2 \cong n_1$) (1)

or
$$1 - \frac{p_1}{p_1^{\circ}} = \frac{W_2 \times M_1}{W_1 \times M_2}$$

Substituting the values, we get

$$1 - \frac{p_1}{23.8} = \frac{50}{60} \times \frac{18}{850} = \frac{3}{170} \implies \frac{p_1}{23.8} = 1 - \frac{3}{170} = \frac{167}{170}$$

$$p_1 = \frac{167 \times 23.8}{170} = \frac{3974.6}{170}$$

$$= 23.38 \text{ mm of Hg}$$
(1)
Relative lowering of vapour pressure}
$$= \frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \frac{23.80 - 23.38}{23.80} = \frac{0.42}{23.80} = 0.018$$
(1)

7 MARK Questions

Important Questions

Q.23 A solution containing 30 g of a 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) the molar mass of the solute.

(ii) the vapour pressure of water at 298 K.

Sol. (i) Suppose the molar mass of solute $= M \text{ g mol}^{-1}$ Number of moles of solute $(n_2) = \frac{30}{M} \text{ mol}$

Number of moles of H_2O

$$(n_{1}) = \frac{90 \text{ g}}{18 \text{ g mol}^{-1}} = 5 \text{ mol}$$

$$p_{1} = 2.8 \text{ kPa}$$

$$\frac{p_{1}^{\circ} - p_{1}}{p_{1}^{\circ}} = \frac{n_{2}}{n_{1} + n_{2}}$$
(1)
$$\frac{p_{1}^{\circ} - 2.8}{p_{1}^{\circ}} = \frac{30/M}{5 + 30/M} \text{ or } 1 - \frac{2.8}{p_{1}^{\circ}} = \frac{30/M}{5 + 30/M}$$
or
$$\frac{2.8}{p_{1}^{\circ}} = 1 - \frac{30/M}{5 + 30/M} = \frac{5}{5 + 30/M}$$
or
$$\frac{p_{1}^{\circ}}{2.8} = \frac{5 + 30/M}{5} = 1 + \frac{6}{M} \qquad \dots (i)_{(1)}$$

On adding 18 g of water,
$$n(H_2O) = 6 \text{ mol}$$

(= 5 + 1 = 6 mol)

Then,
$$p'_1 = 2.9 \text{ kPa}$$

$$\therefore \quad \frac{p_1^{\circ} - 2.9}{p_1^{\circ}} = \frac{30/M}{6 + 30/M}$$

or
$$1 - \frac{2.9}{p_1^{\circ}} = \frac{30/M}{6 + 30/M}$$

or
$$\frac{2.9}{p_1^{\circ}} = 1 - \frac{30/M}{6 + 30/M} = \frac{6}{6 + 30/M}$$

or
$$\frac{p_1^{\circ}}{2.9} = \frac{6 + 30/M}{6} = 1 + \frac{5}{M} \qquad \dots (ii)$$
(1)

On dividing Eq. (i) by Eq. (ii), we get

$$\frac{2.9}{2.8} = \frac{1+6/M}{1+5/M}$$
or $2.9\left(1+\frac{5}{M}\right) = 2.8\left(1+\frac{6}{M}\right)$
or $2.9 + \frac{14.5}{M} = 2.8 + \frac{16.8}{M}$
 $\Rightarrow \qquad M = 23 \text{ u}$ (2)
(ii) Putting $M = 23$ in Eq. (i), we get
 $\frac{p_1^{\circ}}{2.8} = 1 + \frac{6}{23} = \frac{29}{23}$

 $p_1^{\circ} = \frac{29}{23} \times 2.8 = 3.53 \text{ kPa}$ Q.24 Calculate the depression in the freezing point of water when 10g of CH₃CH₂CHClCOOH is added

to 250 g of water. K_a = 1.4 \times 10 $^{-3},$ $K_f = 1.86 \text{ K kg mol}^{-1}$.

- Sol. Molar mass of CH₃CH₂CHClCOOH
 - $= 15 + 14 + 13 + 35.5 + 45 = 122.5 \text{ g mol}^{-1}$ Number of moles of 10 g of CH₃CH₂CHClCOOH

$$n_2 = \frac{10}{122.5} \text{ mol}$$

= 8.16 × 10⁻² mol

TOPIC TEST 4

1. In comparison to 0.01 M solution of glucose, the depression in freezing point of 0.01 M MgCl₂ is (a) the same (b) about twice

((c)	about	three	times	(d)	about	six	times

2. If α is the degree of dissociation of Na_2SO_4 , the van't Hoff factor (i) used for calculating the molecular mass is (a) $1 + 2\alpha$ (b) $1 - 2\alpha$

(u) I	200	(1)	-	200
(c) 1 –	α	(d)	1+	α

[Ans. 1. (c), 2. (a)]

(2)

or

3. Between 2 M glucose solution and 1 M glucose solution, has a lower freezing point.

[Ans. 2M glucose solution]

- 4. Are equimolar solutions of sodium chloride and urea isotonic? Given reason.
- 5. What is the value of van't Hoff factor for 0.1M ideal solution?

:. Molality of the solution (m)

$$= \frac{W_2 \times 1000}{M_2 \times W_1} = \frac{n_2 \times 1000}{W_1}$$

$$= \frac{8.16 \times 10^{-2} \text{ mol}}{250 \text{ g}} \times 1000 \text{ g kg}^{-1}$$

$$= 0.3264 \text{ mol kg}^{-1}$$
(2)
or
$$C = 0.3264 \text{ mol kg}^{-1}$$

or If α is the degree of dissociation for CH₃CH₂CHClCOOH, then $CH_{3}CH_{2}CHClCOOH \Longrightarrow CH_{3}CH_{2}CHClCOO^{-} + H^{+}$ Initial conc. C mol L^{-1} 0 0 At equilibrium $C(1 - \alpha)$ $C\alpha$ Cα $K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} \approx C\alpha^2$ *.*.. (1)

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$$
(1)

 $CH_{3}CH_{2}CHClCOOH \Longrightarrow CH_{3}CH_{2}CHClCOO^{-} + H^{+}$ Initial moles 1 Moles at equilibrium $(1 - \alpha)$ 0 0 α α Total moles = $1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$i = \frac{1+\alpha}{1} = 1+\alpha = 1+0.065 = 1.065$$
 (2)

Therefore, $\Delta T_f = iK_f m$

 $= 1.065 \times 1.86 \times 0.3264 = 0.65^{\circ} \text{ C}$ (1)

- **9.** Four solutions of K_2SO_4 with the concentration 0.1 M, 0.01M, 0.001M and 0.0001M are available. For which concentration, there is maximum value of van't Hoff factor?
- 12. What mass of NaCl must be dissolved in 65.0 g of water to lower the freezing point of water by 7.50°C? The freezing point depression constant (K_f) for water is 1.86°C/m. Assume van't Hoff factor for NaCl is 1.87. (Molar mass of NaCl = 58.5 g mol^{-1}).

15. (i) What is van't Hoff factor?

- (ii) What possible values can it have if the solute molecules undergo dissociation?
- (iii) An aqueous solution containing 12.48 g of barium chloride in 1.0 kg of water boils at 373.0832 K. Calculate the degree of dissociation of barium chloride.

(Given, K_b for $H_2O = 0.52$ K m⁻¹;

molar mass of $BaCl_2 = 208.34 \text{ g mol}^{-1}$).

Chapter Test

1 MARK Questions

1 In which case Raoult's law is not applicable?

(a) 1 M NaCl

- (b) 1 M urea
- (c) 1 M glucose
- (d) 1 M sucrose
- What is the total number of moles of H₂SO₄ required to prepare 5.0 L of a 2.0 M solution of H₂SO₄?
 (a) 10
 (b) 5.0

(~)	10	(~)	0.0
(c)	20	(d)	2.5

[Hint: Number of moles = Molarity × Volume] [Ans. 1.(a), 2.(a)]

- **3** An example of solid solution in which the solute is a gas, is
- 4 State the main advantage of molality over molarity as the unit of concentration.

2 MARK Questions

5 Calculate the mass percentage of a spirin $(C_9H_8O_4)$ in acetonitrile (CH₃CN), when 6.5 g of $C_9H_8O_4$ is dissolved in 540 g of CH₃CN.

Hint Mass % of aspirin

 $= \frac{\text{Mass of aspirin}}{(\text{Mass of aspirin} + \text{Mass of acetonitrile})} \times 100$ [Ans. 1.18%]

- [------
- **6** Why do doctors advise gargles by saline water in case of sore throat?
- 7 What is the molality of a solution in which 18 g glucose (mol. wt. = 180) is dissolved in 500 g of H_2O ?

$$\mathbf{Hint} \text{ Molality} = \frac{\text{Mass of solute}}{\text{Mass of solvent}} \times 100$$

[*Ans*. 0.2 m]

8 Write four differences between solutions having positive deviation and solution having negative deviations from Raoult's laws.

3 MARK Questions

- **9** What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solution?
- **10** Explain with example the concept of minimum boiling azeotropes and maximum boiling azeotropes.
- 11 (i) Why does the use of pressure cooker reduce cooking time?
 - (ii) How does van't Hoff factor help in the determinnation of degree of association or dissociation of a solute in solution.
- 12 (i) If the membrane used for the determination of osmotic pressure is slightly torn, how will it influence the measured value of osmotic pressure?
 - (ii) The boiling point of benzene is 353.23 K. When 1.8 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to be 354.11 K. Calculate the molar mass of the solute, (K_b for benzene is 2.53 K kg mol⁻¹).

Hint Molar mass of solute, $M_2 = \frac{W_2 M_1}{W_1 \left(\frac{p^\circ - p_s}{p^\circ}\right)}$

[Ans. 57.5 kg]

7 MARK Questions

- **13** What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions?
- 14 Calculate the freezing point depression expected for 0.0711 m aqueous solution of Na₂SO₄. If this solution actually freezes at 0.320°C, what would be the values of van't Hoff factor? $(K_p \text{ for water is } 1.86^\circ \text{ C mol}^{-1}).$

Hint van't Hoff equation, $\Delta T_f = iK_f \cdot m$ [Ans. 0.397°C, 2.42]