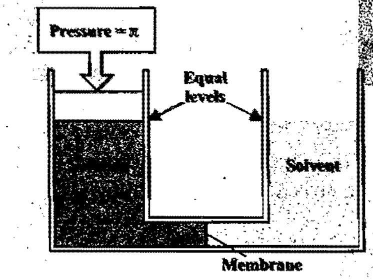


CHAPTER 5

SOLUTIONS

(General and Colligative Properties)

5.1 INTRODUCTION

When two or more chemically non-reacting substances are mixed, they form mixtures. A mixture may be **heterogeneous** or **homogeneous.** A heterogeneous mixture consists of distinct phases and the observed properties are just the sum of the properties of individual phases. However, a homogeneous mixture consists of a single phase which has properties that may differ drastically from those of the individual components.

A homogeneous mixture whose composition can be varied within certain limits is termed a true solution.

The constituents of a solution cannot be separated by filtration, settling or centrifugal action. All solutions are characterised by (i) homogeneity, (ii) absence of settling and (iii) the molecular or ionic state of sub-division of the components.

When the solution is composed of only two chemical substances, it is termed a **binary solution.** Similarly, it is called **ternary** and **quaternary** if it is composed of three and four components, respectively. **Thus, a solution may be regarded as a single phase containing more than one component.**

5.2 SOLVENT AND SOLUTE

Every solution consists of a solvent and one or more solutes. **Solvent in a solution is its constituent substance which has the same state of aggregation as that of the solution.** Generally, the component present in greater amount than any or all the other components is called the solvent. For the solubility of solids in liquids, where the liquid is present in large excess over the solid, there is no ambiguity in these terms, the solid being the solute and the liquid being the solvent. However, if the solution is such that the state of aggregation of the solution is the same as that of a component present in smaller amount, the latter is called the solvent. For example, in a syrup (liquid solution) containing 60% sugar (a solid) and 40% water (a liquid—same aggregation as solution), water is termed as the solvent. In a solution of alcohol and water, the substance present in a larger proportion by mass is called the solvent. But if both the liquids have same masses in solution, it becomes difficult to differentiate between solvent and solute.

5.3 TYPES OF SOLUTIONS

All the three states of matter (gas, liquid or solid) may behave either as solvent or solute. Depending on the state of solute or solvent, mainly there may be the following seven types of binary solutions:

S. No.	Solute	Solvent	Example
1.	Gas	Gas	Air
2.	Gas	Liquid	Aerated water ($CO_2 + H_2O$)
3.	Gas	Solid	Hydrogen in palladium
4.	Liquid	Liquid	Alcohol in water, benzene in toluene
5.	Liquid	Solid	Mercury in zinc amalgam
6.	Solid	Liquid	Sugar in water, common salt in water
7.	Solid	Solid	Various alloys

The solution of liquid in gas or solid in gas is not possible because the constituents cannot form a homogeneous mixture.

For a given solution, the amount of the solute dissolved in a unit volume of solution (or a unit amount of solvent) is termed as the concentration of the solute. Solutions containing relatively high concentration of solute are called **concentrated solutions** while those of relatively low concentration of solute are termed as **dilute solutions.**

In this chapter, we shall discuss only three types of solutions:

(i) Gas in liquid.
(ii) Liquid in liquid.
(iii) Solid in liquid.

5.4 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: It is defined as the amount of solute in gram present in 100 gram of the solution.

$$\text{Mass percentage of solute} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

$$= \frac{\text{Mass of solute}}{\text{Mass of solute} + \text{Mass of solvent}} \times 100$$

$$= \frac{\text{Mass of solute}}{\text{Volume of solution} \times \text{Density of solution}} \times 100$$

The ratio $\frac{\text{Mass of solute}}{\text{Mass of solution}}$ is termed as **mass fraction.**

Thus,

$$\text{Mass percentage of solute} = \text{Mass fraction} \times 100$$

10% solution of sugar means that 10 gram of sugar is present in 100 gram of the solution, *i.e.*, 10 gram of sugar has been dissolved in 90 gram of water.

(ii) Per cent by volume: It is defined as the volume of solute in mL present in 100 mL solution.

$$\text{Per cent of solute by volume} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

(iii) Per cent mass by volume: It is defined as the mass of solute present in 100 mL of solution.

Per cent of solute mass by volume

$$= \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

(iv) Strength or concentration (Gram per litre): It is defined as the amount of the solute in gram present in one litre of the solution.

Concentration of solution

$$= \frac{\text{Mass of solute in gram}}{\text{Volume of the solution in litres}}$$

$$= \frac{\text{Mass of solute in gram}}{\text{Volume of the solution in mL}} \times 1000$$

Concentration in gram per litre is also termed as strength of the solution. Let *w* g of the solute be present in *V* litre of solution, then

$$\text{Strength or concentration of the solution} = \frac{w}{V}\ \text{gL}^{-1}$$

[**Note:** *V* is not the volume of the solvent. *V* is actually the final volume after dissolving a definite quantity of solute in the solvent.]

(v) Parts per million (ppm): When the solute is present in trace quantities, it is convenient to express the concentration in parts per million (ppm). It is defined as the quantity of the solute in gram present in 10^6 gram of the solution.

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

Atmospheric pollution in cities is also expressed in ppm by volume. It refers to the volume of the pollutant in 10^6 units of volume. 10 ppm of SO_2 in air means 10 mL of SO_2 is present in 10^6 mL of air.

(vi) Mole fraction: This method is used when the solution is constituted by mixing two or more components. It is defined as the ratio of number of moles of one component to the total number of moles of the solution (*i.e.*, all the components). Taking three components *A*, *B* and *C*.

Components	A	B	C
Mass (in gram)	w_1	w_2	w_3
Molecular mass	m_1	m_2	m_3
No. of g moles	$\frac{w_1}{m_1}$	$\frac{w_2}{m_2}$	$\frac{w_3}{m_3}$

$$\text{Total number of g moles} = \frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}$$

Thus,

$$\text{Mole fraction of } A = \frac{w_1 / m_1}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}} = f_A$$

$$\text{Mole fraction of } B = \frac{w_2 / m_2}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}} = f_B$$

$$\text{Mole fraction of } C = \frac{w_3 / m_3}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}} = f_C$$

The sum of mole fractions of a solution is equal to 1, *i.e.*,

$$f_A + f_B + f_C = 1$$

In a binary solution,

Mole fraction of solute + Mole fraction of solvent = 1

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

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

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

Thus, $X_A + X_B = 1$

Mole fraction is independent of temperature of the solution.

(vii) Molality: It is defined as the number of moles of the solute present in 1 kg of the solvent. It is denoted by *m*.

$$\text{Molality } (m) = \frac{\text{Number of moles of solute}}{\text{Number of kilo-grams of the solvent}}$$

Let w_B gram of the solute of molecular mass m_B be present in w_A gram of the solvent, then

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

Relation between mole fraction and molality:

$$X_B = \frac{n}{N+n} \text{ and } X_A = \frac{N}{N+n}$$

$$\frac{X_B}{X_A} = \frac{n}{N} = \frac{\text{Moles of solute}}{\text{Moles of solvent}} = \frac{w_B \times m_A}{m_B \times w_A}$$

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

or $$\frac{X_B \times 1000}{(1 - X_B)\, m_A} = m$$

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.

(ii) Molality and solubility are related by the following relation :

$$\text{Molality} = \frac{\text{Solubility} \times 10}{\text{Molecular mass of the solute}}$$

$$\left[\text{Solubility} = \frac{\text{Mass of solute in gram}}{\text{Mass of solvent in gram}} \times 100\right]$$

(viii) Molarity (Molar concentration): It is defined as the number of moles of the solute per litre or per dm^3 of the solution, *i.e.*,

$$\text{Molarity } (M) = \frac{\text{Number of moles of solute}}{\text{Number of litres of solution}}$$

or $$\text{Molarity} \times \text{Number of litres of solution} = \text{Number of moles of solute}$$

Let w_B g of the solute of molecular mass m_B be dissolved in V litre of solution.

$$\text{Molarity of the solution} = \frac{w_B}{m_B \times V}$$

or $$\text{Molarity} \times m_B = \frac{w_B}{V} = \text{Strength of the solution}$$

If V is taken in mL (cm^3), then

$$\text{Molarity of the solution} = \frac{w_B}{m_B \times V} \times 1000$$

The unit of molarity is mol litre^{-1} or mol dm^{-3}.

Molarity (second method): Let d = density of solution in g/mL and let it contains x% solute by mass.

Then, mass of 1 litre solution = $(1000 \times d)$ g

$$\text{Mass of solute in 1 litre} = \frac{x}{100} \times (1000 \times d)\text{ g}$$

$$= (x \times d \times 10)\text{ g}$$

Number of moles of solute in 1 litre

$$= \frac{\text{Mass of solute in gram}}{\text{Gram molecular mass of solute}} = \frac{x \times d \times 10}{m_B}$$

where m_B = molecular mass of solute

$$\therefore \quad \boldsymbol{M = \frac{x \times d \times 10}{m_B}}$$

Molarity of dilution:

Before dilution		*After dilution*
M_1V_1	=	M_2V_2

Molarity of mixing: Let there be three samples of solution (containing same solvent and solute) with their molarity M_1, M_2, M_3 and volumes V_1, V_2, V_3 respectively. These solutions are mixed; molarity of mixed solution may be given as:

$$M_1V_1 + M_2V_2 + M_3V_3 = M_R(V_1 + V_2 + V_3)$$

where, M_R = Resultant molarity

$V_1 + V_2 + V_3$ = Resultant volume after mixing

Note: Molarity is dependent on volume; therefore, it depends on temperature.

1 M	Molar solution, *i.e.*, molarity is 1
0.5 M or $M/2$	Semimolar
0.1 M or $M/10$	Decimolar
0.01 M or $M/100$	Centimolar
0.001 M or $M/1000$	Millimolar

Relationship between molality and molarity:

$$\frac{1}{m} = \frac{\rho}{M} - \frac{m_B}{1000}$$

where, ρ = density of solution

m = molality

M = molarity

m_B = molar mass of solute

Relation between molarity '*M*' and mole fraction:

Let M be the molarity of solution, and x_A, x_B be mole fractions of solvent and solute, respectively.

Suppose n_A and n_B moles of solvent and solute are mixed to form solution.

$$\text{Mass of solution} = n_Am_A + n_Bm_B \qquad \ldots \text{(i)}$$

where, m_A and m_B are molar masses of solvent and solute, respectively.

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{(n_Am_A + n_Bm_B)}{d}$$

$$\text{Molarity} = \text{Number of moles of solute} \times \frac{1000}{\text{Volume of solution}}$$

$$M = n_B \times \frac{1000 \times d}{(n_Am_A + n_Bm_B)}$$

Dividing both numerator and denominator by $(n_A + n_B)$,

$$M = \left\{\frac{n_B}{n_A + n_B}\right\} \times \frac{1000 \times d}{\frac{n_A}{n_A + n_B} \times m_A + \frac{n_B}{n_A + n_B} \times m_B}$$

$$M = \frac{x_B \times 1000 \times d}{x_Am_A + x_Bm_B}$$

(ix) Normality: It is defined as the number of gram equivalents of solute present per litre of solution. It is denoted by '*N*'.

$$\text{Normality } (N) = \frac{\text{Number of gram equivalents of solute}}{\text{Number of litres of the solution}}$$

or **Normality × Number of litres of the solution = Number of gram equivalents of the solute**

Let w_B gram of the solute of equivalent mass E_B be present in V litre of the solution, then,

$$\text{Normality} = \frac{w_B/E_B}{V} = \frac{w_B}{E_B \times V}$$

$$\textbf{Normality} \times \textbf{Equivalent mass} = \frac{w_B}{V}$$

$$= \textbf{Strength of the solution in g/L}$$

Solutions are expressed as:

$$1\,N, 2\,N, \frac{N}{2}, \frac{N}{10}, \frac{N}{100}, \frac{N}{1000}, \text{etc.}$$

Like molarity, normality is also dependent on volume, therefore, it depends on temperature.

Normality of solution may be represented as,

$1\,N$	Normal solution, *i.e.*, normality is 1
$0.5\,N$ or $\frac{N}{2}$	Seminormal
$0.1\,N$ or $\frac{N}{10}$	Decinormal
$0.01\,N$ or $\frac{N}{100}$	Centinormal
$0.001\,N$ or $\frac{N}{1000}$	Millinormal

Relationship between normality and molarity: We know that,

Molarity × Molecular mass = Strength of the solution (g/L)

Similarly,

Normality × Equivalent mass = Strength of the solution (g/L)

Hence,

Molarity × Molecular mass = Normality × Equivalent mass

or
$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular mass}}{\text{Equivalent mass}} = n$$

So, $\textbf{Normality} = n \times \textbf{Molarity}$

[Normality (second method): Let 'd' is the density of solution in g/mL and x is the percentage of the solute by mass. Then,

$$N = \frac{x \times d \times 10}{\text{Equivalent mass of solute}}\ ]$$

(x) Formality: It is the number of formula mass in gram present per litre of solution. In case, formula mass is equal to molecular mass, formality is equal to molarity. Like molarity and normality, the formality is also dependent on temperature. It is used for ionic compounds in which there is no existence of a molecule. Mole of ionic compounds is called **formole** and molarity as **formality.**

SOME SOLVED EXAMPLES

Example 1. *Calculate the masses of cane sugar and water required to prepare 250 g of 25% cane sugar solution.*

Solution: Mass percentage of cane sugar = 25

We know that,

$$\text{Mass percentage} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

So,
$$25 = \frac{\text{Mass of cane sugar}}{250} \times 100$$

or
$$\text{Mass of cane sugar} = \frac{25 \times 250}{100} = 62.5 \text{ g}$$

$$\text{Mass of water} = (250 - 62.5) = 187.5 \text{ g}$$

Example 2. *Calculate the molarity of the following solutions:*

(*a*) *4 g of caustic soda is dissolved in 200 mL of the solution.*

(*b*) *5.3 g of anhydrous sodium carbonate is dissolved in 100 mL of solution.*

(*c*) *0.365 g of pure HCl gas is dissolved in 50 mL of solution.*

Solution: (a) Molecular mass of NaOH = 40

$$\text{No. of gram moles in 4 g of NaOH} = \frac{4}{40} = 0.1$$

$$\text{Volume of solution in litre} = \frac{200}{1000} = 0.2$$

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litre}} = \frac{0.1}{0.2} = 0.5\,M$$

(b) Molecular mass of anhydrous $Na_2CO_3 = 106$

No. of gram moles in 5.3 g of anhydrous Na_2CO_3

$$= \frac{5.3}{106} = 0.05$$

$$\text{Volume of solution in litre} = \frac{100}{1000} = 0.1$$

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

$$= \frac{0.05}{0.1} = 0.5\,M$$

(c) Molecular mass of HCl = 36.5

$$\text{No. of gram moles in 0.365 g of pure HCl} = \frac{0.365}{36.5}$$

$$\text{Volume of solution in litre} = \frac{50}{1000}$$

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

$$= \frac{0.365}{36.5} \times \frac{1000}{50} = 0.2\,M$$

Example 3. *The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/mL. Calculate the molarity and normality of the solution.*

Solution: Volume of 100 g of the solution

$$=\frac{100}{d}=\frac{100}{1.09}\text{ mL}$$
$$=\frac{100}{1.09\times1000}\text{ litre}$$
$$=\frac{1}{1.09\times10}\text{ litre}$$

Number of moles of H_2SO_4 in 100 g of the solution $=\frac{13}{98}$

$$\text{Molarity}=\frac{\text{No. of moles of }H_2SO_4}{\text{Volume of soln. in litre}}=\frac{13}{98}\times\frac{1.09\times10}{1}$$
$$=1.445\,M$$

[**Note:** In solving such numericals, the following formula can be applied:

$$\text{Molarity}=\frac{\%\text{ strength of soln.}\times\text{density of soln.}\times10}{\text{Mol. mass}}$$

Similarly,

$$\text{Normality}=\frac{\%\text{ strength of soln.}\times\text{density of soln.}\times10}{\text{Eq. mass}}\text{]}$$

We know that,

$$\text{Normality}=\text{Molarity}\times n$$
$$=1.445\times2\qquad\left[n=\frac{\text{Mol. mass}}{\text{Eq. mass}}=\frac{98}{49}=2\right]$$
$$=2.89\,N$$

Example 4. *Calculate the molarity of pure water* $(d=1\,g/mL)$.

Solution: Consider 1000 mL of water.

Mass of 1000 mL of water $=1000\times1=1000$ g

No. of moles of water $=\frac{1000}{18}=55.5$

$$\text{Molarity}=\frac{\text{No. of moles of water}}{\text{Volume in litre}}$$
$$=\frac{55.5}{1}=55.5\,M$$

Example 5. *Calculate the quantity of sodium carbonate (anhydrous) required to prepare 250 mL* $\frac{M}{10}$ *solution.*

Solution: We know that,

$$\text{Molarity}=\frac{w}{M\times V}$$

where, w = mass of Na_2CO_3 in g,

M = molecular mass of Na_2CO_3 in gram = 106

V = volume of solution in litre $=\frac{250}{1000}=0.25$

$$\text{Molarity}=\frac{1}{10}$$

Hence, $$\frac{1}{10}=\frac{w}{106\times0.25}$$

or $$w=\frac{106\times0.25}{10}=2.65\text{ g}$$

Example 6. *214.2 g of sugar syrup contains 34.2 g of sugar. Calculate (i) molality of the solution and (ii) mole fraction of sugar in the syrup.*

Solution: (i) Mass of sugar = 34.2 g

$$\text{No. of moles of sugar}=\frac{34.2}{\text{Mol. mass}}=\frac{34.2}{342}=0.1$$

$$\text{Mass of water}=(214.2-34.2)$$
$$=180\text{ g}=\frac{180}{1000}\text{ kg}$$

No. of moles of water $=\frac{180}{18}=10$

$$\therefore\ \text{Molality}=\frac{\text{No. of moles of sugar}}{\text{Mass of water in kg}}=\frac{0.1}{180}\times1000$$
$$=0.555\,m$$

(ii) Total number of moles $=10.0+0.1=10.1$

$$\therefore\ \text{Mole fraction of sugar}=\frac{\text{No. of moles of sugar}}{\text{Total number of moles}}$$
$$=\frac{0.1}{10.1}=0.0099$$

Example 7. *A solution contains 410.3 g of* H_2SO_4 *per litre of solution at 20°C. If the density is 1.243 g/mL, what will be its molarity and molality?*

Solution: Mol. mass of $H_2SO_4=98$

No. of moles of $H_2SO_4=\frac{410.3}{98}=4.186$

$$\text{Molarity of }H_2SO_4\text{ solution}=\frac{\text{No. of moles of }H_2SO_4}{\text{Volume of soln. in litre}}$$
$$=\frac{4.186}{1}=4.186\,M$$

Mass of 1 litre H_2SO_4 solution $=1000\times1.243=1243$ g

Mass of water $=(1243-410.3)=832.7\text{ g}=\frac{832.7}{1000}$ kg

$$\text{Molality of solution}=\frac{\text{No. of moles of }H_2SO_4}{\text{Mass of water in kg}}$$
$$=\frac{4.186}{832.7}\times1000$$
$$=5.027\,m$$

Example 8. *The density of a 2.03 M solution of acetic acid (molecular mass 60) in water is 1.017 g/mL. Calculate the molality of the solution.*

Solution: Strength of the solution

$$= \text{Molarity} \times \text{mol. mass}$$
$$= 2.03 \times 60 = 121.8 \text{ g/L}$$

Density of solution $= 1.017$ g/mL

Mass of 1 litre of solution $= 1000 \text{ mL} \times 1.017 \text{ g/mL}$
$$= 1017 \text{ g}$$

Mass of water $= 1017 - 121.8 = 895.2 \text{ g} = \frac{895.2}{1000}$ kg

$$\text{Molality} = \frac{2.03}{895.2} \times 1000 = 2.267\ m$$

Example 9. *The density of a 3 M sodium thiosulphate solution ($Na_2S_2O_3$) 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 $S_2O_3^{2-}$ ions.*

Solution: (i) Mass of 1000 mL of $Na_2S_2O_3$ solution

$$= 1.25 \times 1000 = 1250 \text{ g}$$

Mass of $Na_2S_2O_3$ in 1000 mL of 3 *M* solution

$$= 3 \times \text{Mol. mass of } Na_2S_2O_3$$
$$= 3 \times 158 = 474 \text{ g}$$

Mass percentage of $Na_2S_2O_3$ in solution

$$= \frac{474}{1250} \times 100 = 37.92$$

Alternatively, $M = \dfrac{x \times d \times 10}{m_A}$

$$3 = \frac{x \times 1.25 \times 10}{158}$$

$$x = 37.92$$

(ii) No. of moles of $Na_2S_2O_3 = \dfrac{474}{158} = 3$

Mass of water $= (1250 - 474) = 776$ g

No. of moles of water $= \dfrac{776}{18} = 43.1$

Mole fraction of $Na_2S_2O_3 = \dfrac{3}{43.1 + 3} = \dfrac{3}{46.1} = 0.065$

(iii) No. of moles of Na^+ ions

$$= 2 \times \text{No. of moles of } Na_2S_2O_3$$
$$= 2 \times 3 = 6$$

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

$$= \frac{6}{776} \times 1000$$

$$= 7.73\ m$$

No. of moles of $S_2O_3^{2-}$ ions = No. of moles of $Na_2S_2O_3$

$$= 3$$

$$\text{Molality of } S_2O_3^{2-} \text{ ions} = \frac{3}{776} \times 1000 = 3.86\ m$$

Example 10. *A solution is prepared by dissolving 5.64 g of glucose in 60 g of water. Calculate the following:*

(i) mass per cent of each of glucose and water,
(ii) molality of the solution,
(iii) mole fraction of each of glucose and water.

Solution: (i) Total mass of solution

$$= 5.64 + 60 = 65.64 \text{ g}$$

$$\text{Mass per cent of glucose} = \frac{5.64}{65.64} \times 100 = 8.59\%$$

Mass per cent of water = (100 – Mass per cent of glucose)
$$= (100 - 8.59) = 91.41\%$$

(ii) No. of moles of glucose $= \dfrac{5.64}{180}$

Mass of water in kg $= \dfrac{60}{1000}$

$$\text{Molality} = \frac{5.64}{180} \times \frac{1000}{60} = 0.522\ m$$

(iii) No. of moles of glucose $= \dfrac{5.64}{180} = 0.0313$

No. of moles of water $= \dfrac{60}{18} = 3.333$

$$\text{Mole fraction of glucose} = \frac{0.0313}{3.333 + 0.0313} = 0.0093$$

$$\text{Mole fraction of water} = \frac{3.333}{3.333 + 0.0313} = 0.9907$$

Example 11. *What would be the molality of a solution made by mixing equal volumes of 30.0% by mass of H_2SO_4 (density 1.218 g cm^{-3}) and 70% by mass of H_2SO_4 (density 1.610 g cm^{-3})?*

Solution: Let 100 mL of one solution be mixed with 100 mL of the other solution.

Mass of 100 mL of 30% $H_2SO_4 = 100 \times 1.218 = 121.8$ g

Mass of H_2SO_4 in 121.8 g of 30% H_2SO_4

$$= \frac{30}{100} \times 121.8 \text{ g} = 36.54 \text{ g}$$

Mass of water $= (121.8 - 36.54) = 85.26$ g

Mass of 100 mL of 70% $H_2SO_4 = 100 \times 1.61 = 161.0$ g

Mass of H_2SO_4 in 161.0 g of 70% H_2SO_4

$$= \frac{70}{100} \times 161.0 \text{ g} = 112.7 \text{ g}$$

Mass of water $= (161.0 - 112.7) = 48.30$ g

Total H_2SO_4 in solution $= 36.54 + 112.7 = 149.24$ g

$$\text{No. of moles of } H_2SO_4 = \frac{149.24}{98}$$

$$\text{Total mass of water in solution} = (85.26 + 48.30)$$

$$= 133.56\text{ g} = \frac{133.56}{1000}\text{ kg}$$

$$\text{Molality} = \frac{\text{No. of moles of } H_2SO_4}{\text{Mass of water in kg}} = \frac{149.24}{98} \times \frac{1000}{133.56}$$

$$= 11.4\ m$$

Example 12. *The mole fraction of CH_3OH in an aqueous solution is 0.02 and its density is 0.994 g cm^{-3}. Determine its molarity and molality.*

Solution: Let x mole of CH_3OH and y mole of water be present in solution.

$$\text{Mole fraction of } CH_3OH = \frac{x}{x+y} = 0.02$$

$$\text{So,} \quad \frac{y}{x} = 49 \quad \text{or} \quad \frac{x}{y} = \frac{1}{49}$$

$$\text{Molality} = \frac{x}{18 \times y} \times 1000 = \frac{1000}{18 \times 49} = 1.13\ m$$

$$\text{Volume of solution} = \frac{\text{Total mass}}{\text{density}} = \frac{32x + 18y}{0.994}\text{ mL}$$

$$= \frac{32x + 18y}{0.994 \times 1000}\text{ litre} = \frac{32x + 18y}{994}\text{ litre}$$

$$\text{Molarity} = \frac{x}{32x + 18y} \times 994$$

$$= \frac{994}{32 + 18 \times y/x} = \frac{994}{32 + 18 \times 49} = 1.0875\ M$$

Example 13. *Calculate the concentration of NaOH solution in g/mL, which has the same normality as that of a solution of HCl of concentration 0.04 g/mL.*

Solution:

$$N_{\text{HCl}} = \frac{w_B \times 1000}{E_B \times V} = \frac{0.04 \times 1000}{36.5 \times 1} = 1.095$$

$$N_{\text{NaOH}} \equiv N_{\text{HCl}}$$

$$\therefore \quad 1.095 = \frac{w_B \times 1000}{40 \times 1}$$

$$w_B = 0.0438\text{ g/mL}$$

Example 14. *How many Na^+ ions are present in 50 mL of a 0.5 M solution of NaCl?*

Solution:

$$\text{Number of moles of NaCl} = \frac{MV}{1000}$$

$$= \frac{0.5 \times 50}{1000} = 0.025$$

$$NaCl \longrightarrow Na^+ + Cl^-$$

$$\text{Number of moles of } Na^+ = \text{Number of moles of NaCl}$$

$$= 0.025$$

$$\text{Number of ions of } Na^+ = 0.025 \times 6.023 \times 10^{23}$$

$$= 1.505 \times 10^{22}$$

Example 15. *Reaction,*

$$2Br^-(aq) + Cl_2(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$$

is used for commercial preparation of bromine from its salts. Suppose we have 50 mL of a 0.06 M solution of NaBr. What volume of a 0.05 M solution of Cl_2 is needed to react completely with the Br^-?

Solution: $2Br^-(aq) + Cl_2(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$

$$\frac{M_1V_1(Br^-)}{n_1} = \frac{M_2V_2(Cl_2)}{n_2}$$

where, n_1 and n_2 are corresponding coefficients.

$$\therefore \quad \frac{0.06 \times 50}{2} = \frac{0.05 \times V_2}{1}$$

$$\therefore \quad V_2 = 30\text{ mL}$$

Example 16. *Calculate the molarity, molality and mole fraction of ethyl alcohol in a solution of total volume 95 mL prepared by adding 50 mL of ethyl alcohol (density = 0.789 mL^{-1}) to 50 mL water (density = 1.00 g mL^{-1}).*

Solution:

$$\text{No. of moles of ethyl alcohol} = \frac{\text{Vol.} \times \text{density}}{\text{Mol. mass}}$$

$$= \frac{50 \times 0.789}{46} = 0.8576$$

$$\text{No. of moles of water} = \frac{\text{Vol.} \times \text{density}}{\text{Mol. mass}} = \frac{50 \times 1}{18}$$

$$= 2.7777$$

$$\text{Molarity} = \frac{\text{No. of moles}}{\text{Vol. of sol. in mL}} \times 1000$$

$$= \frac{0.8576}{95} \times 1000 = 9.027\ M$$

$$\text{Molality} = \frac{\text{No. of moles of [illegible]ute}}{\text{Mass of solvent [illegible]rams}} \times 1000$$

$$= \frac{0.8576}{50} \times 1000 = \text{[illegible]}52\ m$$

$$\text{Mole fraction} = \frac{0.8576}{0.8576 + 2.7777} = \frac{0.8576}{3.6353} = 0.236$$

5.5 SOLUTIONS OF GASES IN LIQUIDS (Solubility of Gases)

All gases are soluble in water as well as in other liquids to a greater or lesser extent. Solutions of gases in water play an important role in our daily life. The common examples are carborated beverages, *i.e.*, soft drinks, household cleaners containing aqueous solutions of ammonia, formalin-an aqueous solution of formaldehyde, etc. The natural waters contain dissolved O_2 which is vital for the existence of aquatic life in sea, rivers and lakes.

The solubility of a gas in a liquid is expressed in terms of **absorption coefficient.** It is defined as the volume of the gas in mL that can be dissolved by 1 mL of a liquid solvent at the temperature of the experiment at one atmospheric pressure. The volume of the gas is measured at STP. Thus, if v is the volume of the gas dissolved, reduced to STP, V is the volume of the solvent and P is pressure of the gas in atmospheres, then the absorption coefficient, α, is given by

$$\alpha = \frac{v}{VP}$$

The following factors affect the solubilities of gases in liquids:

(i) Nature of the gas and solvent : Generally, the gases which can be easily liquefied are more soluble in common solvents. For example, CO_2 is more soluble in water than oxygen or hydrogen. The gases which react with the solvent posses higher solubility. For example, HCl and NH_3 are highly soluble in water.

Oxygen, nitrogen and carbon dioxide are much more soluble in ethyl alcohol than in water at the same temperature and pressure.

(ii) Temperature : The solubility of most of the gases in liquids decreases with increase of temperature as the dissolution is an exothermic process. When water is heated in a beaker, bubbles of air are formed on the sides of the glass before the water boils. As the temperature rises, the dissolved air molecules begin to "boil out" of the solution long before the water itself boils.

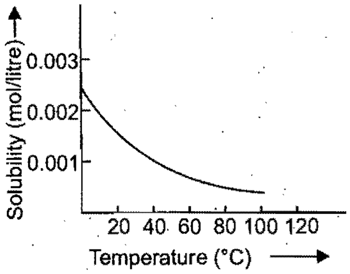


Fig. 5.1 Temperature dependence of O_2 gas solubility in water

The reduced solubility of molecular oxygen in hot water has a direct bearing on **thermal pollution,** *i.e., the heating of the environment*—usually waterways—*to temperatures that are harmful to its living inhibitants.*

(iii) Pressure : The most important factor which influences the solubility of a gas in a liquid is the **pressure.** The effect of pressure on the solubility of the gas in the liquid is given by Henry's law, which states that *the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution at a definite temperature.* The solubility is taken as the mass of the gas dissolved per unit volume of the liquid. Thus, if m is the mass of the gas dissolved per unit volume of the solvent and P is the pressure of the gas in equilibrium with the solution, then

$$m \propto P$$

or

$$m = KP \qquad \text{...(i)}$$

where, K is the proportionality constant.

When $P = 1$, $m = K$, *i.e.*, the solubility of the gas at unit pressure is equal to constant K. The value of K is different for each gas at a particular temperature. The magnitude of K depends upon the nature of the gas, nature of solvent, temperature and the units of pressure. Equation (i) represents equation of straight line $(y = mx)$ passing through origin. Fig. 5.2 shows the variation of solubility of some gases against equilibrium pressure. The straight line graphs show the validity of Henry's law.

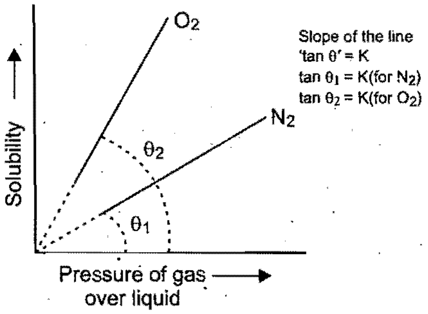


Fig. 5.2 Variation of solubility of a gas with pressure

If solubility of the gas is known at one particular pressure, then it can be calculated at other pressures using the following relation,

$$\frac{m_1}{m_2} = \frac{P_1}{P_2} \qquad \text{...(ii)}$$

where 'm_1' is the solubility of the gas at pressure 'P_1' and 'm_2' is the solubility of the gas at pressure 'P_2'.

When a mixture of two or more non-reacting gases is brought in contact with a solvent, each constituent gas dissolves in proportion to its own partial pressure. Henry's law can be applied to each individual gas independent of the presence of other gas. If we use the mole fraction of the gas in the solution as a measure of its solubility, then the law can be stated as, "*mole fraction of the gas in a solution is proportional to the partial pressure of the gas.*"

$$x \propto P$$

where, x = mole fraction of the gas in solution

and p = partial pressure of the gas.

or $x = K' p$

or $$p = \frac{1}{K'} x = K_H x \qquad \left(K_H = \frac{1}{K'}\right) \text{...(iii)}$$

K_H is called Henry's law constant. Different gases have different values of K_H at a definite temperature for a given solvent.

Table 5.1 Values of Henry's Law Constant (K_H) for Some Common Gases in Water

Gas	Temperature (K)	K_H (k bar)
He	293	144.97
H_2	293	69.16
N_2	293	76.48
N_2	303	88.84
O_2	293	34.86
O_2	393	46.82

From equation (iii), it can be inferred that higher is the value of Henry's law constant, the lower is the solubility of the gas in the liquid.

Limitations of Henry's Law

Henry's law holds good if the following conditions are fulfilled :

(i) The pressure is not too high,

(ii) The temperature is not very low,

(iii) The gas does not chemically combine with the solvent.

The gas molecules do not either dissociate or associate in the solvent. In case the dissolved gas reacts with the solvent, higher solubilities can result. The solubility of ammonia in water is much higher than expected because of the following reaction :

$$NH_3 + H_2O = NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Carbon dioxide also reacts with water.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Another interesting example concerns the dissolution of oxygen in blood. Normally, oxygen gas is only sparingly soluble in water. However, its solubility in blood is abnormally high because of the high content of haemoglobin (Hb) molecules, which are eventually delivered to the tissues for use in metabolism.

$$Hb + 4O_2 \rightleftharpoons Hb\,(O_2)_4$$

Due to these processes, Henry's law is not strictly followed.

Applications of Henry's Law

1. Soft drink bottles are sealed at high pressure, to increase the solubility of CO_2 in the soft drink.

2. At high altitude, partial pressure of oxygen is low, it leads to low concentration of oxygen in blood of people living there. Low concentration of oxygen develops **anoxia,** *i.e.*, unable to think and act properly.

3. When scuba divers go deep in the sea, solubility of atmospheric gases increases in blood. When the divers come up, there is release of dissolved gases and it leads to the formation of bubbles of nitrogen in our blood capillaries and hence there is painful sensation called **bends.** To avoid bends; the tanks of scuba divers are filled with 11.7% He, 56.2% N_2 and 32.1% oxygen.

[**Note :** (i) Gases are less soluble in aqueous solutions of electrolytes than in pure water. It is called *salting out effect.*

(ii) Non-electrolytes such as sugar if present in a solution also reduce the solubility of gases in water.]

Example 17. *Calculate the concentration of CO_2 in a soft drink that is bottled at partial pressure of CO_2 of 4 atm over the liquid at 25° C. The Henry's Law constant for CO_2 in water at 25° C is 3.1×10^{-2} mol/litre-atm.*

Solution: According to Henry's Law:

$$S = KP = 3.1 \times 10^{-2} \times 4 = 0.12 \text{ mol litre}^{-1}$$

Example 18. *The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5×10^{-2} g of ethane, then what shall be the partial pressure of the gas?*

Solution:

$$\frac{S_1}{S_2} = \frac{P_1}{P_2}$$

$$\frac{6.56 \times 10^{-2}}{5 \times 10^{-2}} = \frac{1}{P_2}$$

$$P_2 = 0.762 \text{ bar}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. 0.5 M H_2SO_4 is diluted from 1 litre to 10 litre, normality of the resulting solution is: (AFMC 2005)

(a) 1 N (b) 0.1 N (c) 10 N (d) 11 N

[**Ans.** (b)]

[**Hint:** $M_1V_1 = M_2V_2$

$$0.5 \times 1 = M_2 \times 10$$

$$M_2 = 0.05$$

$N = M \times$ basicity of acid $= 0.05 \times 2 = 0.1\,N$]

2. Molar solution means 1 mole of solute present in: [BCECE (Medical) 2005]

(a) 1000 g of solvent (b) 1 litre of solvent

(c) 1 litre of solution (d) 1000 g of solution

[**Ans.** (c)]

3. The molarity of a solution containing 50 g of NaCl in 500 g of a solution and having a density of 0.936 g/cm^3 is:

(a) 1.5 M (b) 1.6 M (c) 1.8 M (d) 1.2 M

[**Ans.** (b)]

[**Hint:** $M = \dfrac{x \times d \times 10}{m_B}$ ... (i)

$$x = \frac{50}{500} \times 100 = 10$$

$\therefore$ $M = \dfrac{10 \times 0.936 \times 10}{58.5} = 1.6\,M$]

4. 20 mL of 0.5 M HCl is mixed with 30 mL of 0.3 M HCl, the molarity of the resulting solution is:

(a) 0.8 M (b) 0.53 M (c) 0.38 M (d) 0.83 M

[**Ans.** (c)]

[**Hint:** $M_1V_1 + M_2V_2 = M_R(V_1 +$

$$0.5 \times 20 + 0.3 \times 30 = M_R \times 5$$

$$M_R = 0.38\,M$$

where, M_R = resultant molarity o mixture.]

5. How many moles and how many grams of NaCl are present in 250 mL of a 0.5 M NaCl solution?

(a) 0.125 mol; 7.32 g (b) 7.32 mol; 0.125 g

(c) 0.125 mol; 0.125 g (d) 7.32 mol; 7.32 g

[**Ans.** (a)]

[**Hint:** Number of moles $= \dfrac{MV}{1000} = \dfrac{0.5 \times 250}{1000} = 0.125$

Mass of NaCl = 58.5 × 0.125 = 7.32 g]

6. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is: (AIEEE 2006)

(a) 1.14 mol kg^{-1} (b) 3.28 mol kg^{-1}

(c) 2.28 mol kg^{-1} (d) 0.44 mol kg^{-1}

[**Ans.** (c)]

[**Hint:** $m = \dfrac{M \times 1000}{1000d - Mm_B} = \dfrac{2.05 \times 1000}{1000 \times 1.02 - 2.05 \times 60}$

$= 2.28$ mol kg^{-1}]

7. The hardness of water sample containing 0.002 mol of magnesium sulphate dissolved in a litre of water is expressed as: [PET (Kerala) 2007]

(a) 20 ppm (b) 200 ppm (c) 2000 ppm (d) 120 ppm
(e) 240 ppm

[**Ans.** (b)]

[**Hint:** 10^6 g water contains (0.002×1000) mol $MgSO_4$

$1 \text{ mol } MgSO_4 \cong 1 \text{ mol } CaCO_3$

$\therefore \quad 2 \text{ mol } MgSO_4 \cong 2 \text{ mol } CaCO_3$, *i.e.*, 2×100 g $CaCO_3$

$\therefore$ Hardness of water = 200 ppm]

8. The density (in g mL^{-1}) of a 3.6 M sulphuric acid solution, *i.e.*, 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be: (AIEEE 2007)

(a) 1.45 (b) 1.64 (c) 1.88 (d) 1.22

[**Ans.** (d)]

[**Hint:** $M = \dfrac{x \times d \times 10}{m_B}$

$$d = \frac{M \times m_B}{x \times 10} = \frac{3.6 \times 98}{29 \times 10} \approx 1.22 \text{ g mL}^{-1}]$$

9. 1 litre solution containing 490 g of sulphuric acid is diluted to 10 litre with water. What is the normality of the resulting solution? (SCRA 2007)

(a) 0.5 N (b) 1.0 N (c) 5.0 N (d) 10.0 N

[**Ans.** (b)]

[**Hint:** $N = \dfrac{w_B \times 1000}{E_B \times V} = \dfrac{490 \times 1000}{49 \times 1000} = 10$

$N_1V_1 = N_2V_2$
$10 \times 1 = N_2 \times 10$
$N_2 = 1$]

10. 250 mL of a Na_2CO_3 solution contains 2.65 g of Na_2CO_3. 10 mL of this solution is added to x mL of water to obtain 0.001 M Na_2CO_3 solution. The value of x is....
(Molecular mass of Na_2CO_3 = 106 amu) [BHU (Mains) 2008]

(a) 1000 (b) 990 (c) 9990 (d) 90

[**Ans.** (b)]

[**Hint :** Molarity of solution.

$$M = \frac{w_B \times 1000}{m_B \times V} = \frac{2.65 \times 1000}{106 \times 250} = 0.1$$

$M_1V_1 = M_2V_2$
$0.1 \times 10 = 0.001\,(10 + x)$
$x = 990$ mL]

11. The volumes of two HCl solutions A (0.5 N) and B (0.1 N) to be mixed for preparing 2 L of 0.2 N HCl are : [EAMCET (Med) 2008]

(a) 0.5 L of A + 1.5 L of B
(b) 1.5 L of A + 0.5 L of B
(c) 1 L of A + 1 L of B
(d) 0.75 L of A + 1.25 L of B

[**Ans.** (a)]

[**Hint :** Let x L of A and $(2 - x)$ L of B are mixed.

$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$
$0.5 \times x + 0.1\,(2 - x) = 0.2 \times 2$
$(0.5 - 0.1)\,x = 0.4 - 0.2$
$0.4\,x = 0.2$
$x = 0.5$ L

$\therefore$ 0.5 L of A and 1.5 L of B should be mixed.]

5.6 SOLUTIONS OF LIQUIDS IN LIQUIDS

When one liquid dissolves in another, the molecules of the solvent are caused to move apart so as to accommodate the solute molecules. Similarly, the solute molecules must also be separated so that they can take their places in the mixture. In both these processes, energy is required. Finally, as the solute and solvent molecules are brought together, energy is released because of the attractive forces between them. When solute and solvent molecules are strongly attracted to each other, more energy is released in the final step. Three cases may arise under these circumstances. The overall dissolution process results either in evolution of heat or absorption of heat, or energy released in the final step is the same as the energy absorbed in the first two, *i.e.*, net change is zero.

Examples:

1. Benzene and carbon tetrachloride:	No evolution or absorption of heat.
2. Acetone and water:	Evolution of heat.
3. Ethyl alcohol and water:	Absorption of heat.

A liquid may or may not be soluble in another liquid. Depending upon the relative solubility of a liquid in another, the following three cases are possible:

Liquid-Liquid Systems

1. Liquids that are completely miscible.	2. Liquids that are partially miscible.	3. Liquids that are practically immiscible.
Examples: Benzene and toluene; Ethyl alcohol and water; Carbon tetrachloride and benzene.	*Examples*: Ether and water; Phenol and water; Nicotine and water.	*Examples*: Benzene and water; Carbon tetrachloride and water; Benzene and alcohol.

Miscible liquids form three types of solutions, which can be ideal or non-ideal solutions.

Ideal solution: An ideal solution is one in which the molecules attract one another with equal force irrespective of their nature. Thus, a solution composed of two components A and B will be an ideal one if the forces between A and A, B and B should be the same. An ideal solution possesses the following characteristics:

(i) Volume change of mixing should be zero.

$$\Delta V_{\text{mix}} = 0; \quad V_{\text{solvent}} + V_{\text{solute}} = V_{\text{solution}}$$

(ii) Heat change on mixing should be zero.

$$\Delta H_{\text{mix}} = 0 \text{ (Heat is neither absorbed nor evolved.)}$$

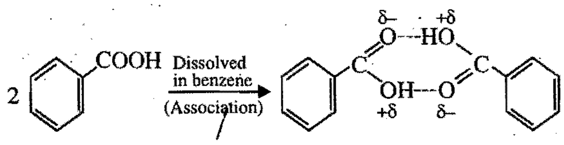
(iii) There should be no chemical reaction between solvent and solute.

$$\left.\begin{array}{lll} \text{Solvent} + & \text{Solute} & \longrightarrow \text{Solution} \\ H_2O & + NH_3 & \longrightarrow NH_4OH \\ H_2O & + CO_2 & \longrightarrow H_2CO_3 \\ H_2O & + CaO & \longrightarrow Ca(OH)_2 \end{array}\right\} \text{Non-ideal}$$

(iv) Solute molecules should not dissociate in the ideal solution.

$$\left.\begin{array}{l} NaCl \xrightarrow{\text{Aqueous medium}} Na^+ + Cl^- \\ H_2SO_4 \xrightarrow{\text{Aqueous medium}} 2H^+ + SO_4^{2-} \end{array}\right\} \text{Non-ideal}$$

(v) Solute molecules should not associate in ideal solution.



Non-ideal

(vi) Ideal solutions must obey Raoult's law at all concentrations.

The following are some of the binary mixtures which show the properties of ideal solutions:

(a) Benzene and toluene,

(b) Carbon tetrachloride and silicon tetrachloride,

(c) *n*-Hexane and *n*-heptane,

(d) Ethylene dibromide and ethylene dichloride.

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.**

Let a mixture (solution) be prepared by mixing n_A mole of liquid A and n_B mole of liquid B. Let p_A and p_B be the partial pressures of two constituents A and B in solution and p_A^0 and p_B^0 the vapour pressures in pure state respectively.

Table 5.2 Comparison between Ideal and Non-ideal Solutions

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	**Negative deviation from Raoult's law**
1. Obey Raoult's law at every range of concentration.	Do not obey Raoult's law.	Do not obey Raoult's law.
2. $\Delta H_{mix} = 0$; neither heat is evolved nor absorbed during dissolution.	$\Delta H_{mix} > 0$. Endothermic dissolution; heat is absorbed.	$\Delta H_{mix} < 0$. Exothermic dissolution; heat is evolved.
3. $\Delta V_{mix} = 0$; total volume of solution is equal to sum of volumes of the components.	$\Delta V_{mix} > 0$. Volume is increased after dissolution.	$\Delta V_{mix} < 0$. Volume is decreased during dissolution.
4. $P = p_A + p_B = p_A^0 X_A + p_B^0 X_B$ *i.e.*, $p_A = p_A^0 X_A$; $p_B = p_B^0 X_B$	$p_A > p_A^0 X_A$; $p_B > p_B^0 X_B$ $\therefore p_A + p_B > p_A^0 X_A + p_B^0 X_B$	$p_A < p_A^0 X_A$; $p_B < p_B^0 X_B$ $\therefore p_A + p_B < p_A^0 X_A + p_B^0 X_B$
5. $A — A$, $A — B$, $B — B$ interactions should be same, *i.e.*, 'A' and 'B' are identical in shape, size and character.	$A — B$ attractive force should be weaker than $A — A$ and $B — B$ attractive forces. 'A' and 'B' have different shape, size and character.	$A — B$ attractive force should be greater than $A — A$ and $B — B$ attractive forces. 'A' and 'B' have different shape, size and character.
6. Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.	'A' and 'B' escape easily showing higher vapour pressure than the expected value.	Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.
Examples: dilute solutions; benzene + toluene; *n*-hexane + *n*-heptane; chlorobenzene + bromobenzene; ethyl bromide + ethyl iodide; *n*-butyl chloride + *n*-butyl bromide.	**Examples:** acetone + ethanol; acetone + CS_2; water + methanol; water + ethanol; CCl_4 + toluene; CCl_4 + $CHCl_3$; acetone + benzene; CCl_4 + CH_3OH; cyclohexane + ethanol.	**Examples:** acetone + aniline; acetone + chloroform; CH_3OH + CH_3COOH; H_2O + HNO_3; chloroform + diethyl ether; water + HCl; acetic acid + pyridine; chloroform + benzene.

Thus, according to Raoult's law,

$$p_A = \frac{n_A}{n_A + n_B}\, p_A^0 = \text{mole fraction of } A \times p_A^0 = X_A\, p_A^0$$

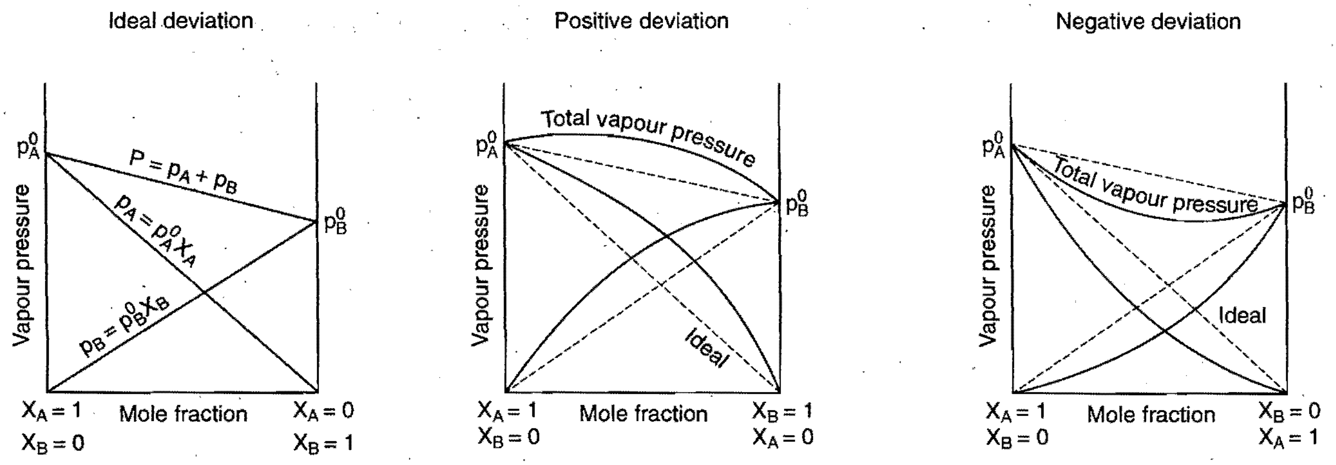
and $$p_B = \frac{n_B}{n_A + n_B}\, p_B^0 = \text{mole fraction of } B \times p_B^0 = X_B\, p_B^0$$

If the total pressure be P, then

$$P = p_A + p_B$$
$$= \frac{n_A}{n_A + n_B}\, p_A^0 + \frac{n_B}{n_A + n_B}\, p_B^0$$
$$= X_A\, p_A^0 + X_B\, p_B^0$$

This law, in fact, is the major deciding factor, whether a solution will be ideal or non-ideal. Ideal solutions obey Raoult's law at every range of concentration. Non-ideal solutions do not obey Raoult's law. They show either **positive** or **negative** deviation from Raoult's law. For comparison between ideal and non-ideal solutions a table has been given below. (Only binary combinations of miscible liquids have been considered.)

Graphical Representation of Ideal and Non-ideal Solutions



Ideal deviation

Positive deviation

Negative deviation

Fig. 5.3

Relation between Dalton's Law and 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 pressures of vapours A and B respectively and total pressure P.

$$p_A = Y_A\, P \qquad \text{... (i)}$$
$$p_B = Y_B\, P \qquad \text{... (ii)}$$
$$p_A = X_A\, p_A^0 \qquad \text{... (iii)}$$
$$p_B = X_B\, p_B^0 \qquad \text{... (iv)}$$

Equating eqs. (i) and (iii),

$$Y_A\, P = X_A\, p_A^0$$

or $$Y_A = \frac{X_A\, p_A^0}{P} = \frac{p_A}{P}$$

Similarly, equating eqs. (ii) and (iv),

$$Y_B = \frac{X_B\, p_B^0}{P} = \frac{p_B}{P}$$

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

Example 19. *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: Mol. mass of ethyl alcohol = $C_2H_5OH = 46$

$$\text{No. of moles of ethyl alcohol} = \frac{60}{46} = 1.304$$

Mol. mass of methyl alcohol = $CH_3OH = 32$

$$\text{No. of moles of methyl alcohol} = \frac{40}{32} = 1.25$$

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

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

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

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

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

Mole fraction of methyl alcohol in the vapour

$$= \frac{\text{Partial pressure of } CH_3OH}{\text{Total vapour pressure}} = \frac{43.40}{66.13} = 0.6563$$

Example 20. *Two liquids A and B form an ideal solution. At 300K, the vapour pressure of a solution containing 1 mole of A and 3 mole of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.*

Solution: Let the vapour pressure of pure A be $= p_A^0$; and the vapour pressure of pure B be $= p_B^0$.

Total vapour pressure of solution (1 mole A + 3 mole B)

$$= X_A \cdot p_A^0 + X_B \cdot p_B^0 \quad [X_A \text{ is mole fraction of } A \text{ and } X_B \text{ is mole fraction of } B]$$

$$550 = \frac{1}{4} p_A^0 + \frac{3}{4} p_B^0$$

or $$2200 = p_A^0 + 3p_B^0 \qquad \ldots \text{(i)}$$

Total vapour pressure of solution (1 mole A + 4 mole B)

$$= \frac{1}{5} p_A^0 + \frac{4}{5} p_B^0$$

$$560 = \frac{1}{5} p_A^0 + \frac{4}{5} p_B^0$$

or $$2800 = p_A^0 + 4p_B^0 \qquad \ldots \text{(ii)}$$

Solving eqs. (i) and (ii),

$p_B^0 = 600$ mm of Hg = vapour pressure of pure B

$p_A^0 = 400$ mm of Hg = vapour pressure of pure A

Example 21. *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_{total} = Mole fraction of $A \times p_A^0$ + Mole fraction of $B \times p_B^0$

No. of moles of $A = \frac{28}{140} = 0.2$

Liquid B is water. Its mass is $(100 - 28)$, *i.e.*, 72.

No. of moles of $B = \frac{72}{18} = 4.0$

Total no. of moles $= 0.2 + 4.0 = 4.2$

Given, $P_{\text{total}} = 160$ mm

$p_B^0 = 150$ mm

So, $$160 = \frac{0.2}{4.2} \times p_A^0 + \frac{4.0}{4.2} \times 150$$

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

Example 22. *Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquids are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure, in bar, of a mixture of 25 g of heptane and 35 g of octane?*

Solution: (A) Heptane C_7H_{16} $m_A = 100$

(B) Octane C_8H_{18} $m_B = 114$

$$n_A = \frac{w_A}{m_A} = \frac{25}{100} = 0.25; \quad n_B = \frac{35}{114} = 0.3$$

$$x_A = \frac{0.25}{0.25 + 0.30} = 0.45; \qquad x_B = \frac{0.3}{0.25 + 0.30} = 0.55$$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 105.2 \times 0.45 + 46.8 \times 0.55$$

$$= 47.34 + 25.74 = 73.08 \text{ kPa}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

12. Mole fraction of the component A in vapour phase is x_1 and the mole fraction of component A in liquid mixture is x_2, then (p_A^0 = vapour pressure of pure A; p_B^0 = vapour pressure of pure B), the total vapour pressure of liquid mixture is:

(a) $p_A^0 \frac{x_2}{x_1}$ (b) $p_A^0 \frac{x_1}{x_2}$ (c) $p_B^0 \frac{x_1}{x_2}$ (d) $p_B^0 \frac{x_2}{x_1}$

[Ans. (a)]

[Hint: $p_A = p_A^0 x_2$, vapour pressure of 'A'

Mole fraction of A in vapour $= \frac{p_A}{p_{\text{total}}}$

$$x_1 = \frac{p_A^0 x_2}{p}$$

$$p = \frac{p_A^0 x_2}{x_1}]$$

13. Vapour pressure of pure A (p_A^0) = 100 mm Hg

Vapour pressure of pure B (p_B^0) = 150 mm Hg

2 mole of liquid A and 3 mole of liquid B are mixed to form an ideal solution. The vapour pressure of solution will be:

(a) 135 mm (b) 130 mm (c) 140 mm (d) 145 mm

[Ans. (b)]

[Hint: $x_A = \frac{2}{5}, x_B = \frac{3}{5}$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 100 \times \frac{2}{5} + 150 \times \frac{3}{5} = 40 + 90 = 130]$$

14. The vapour pressure of a certain pure liquid A at 298 K is 40 m bar. When a solution of B is prepared in A at the same temperature, the vapour pressure is found to be 32 m bar. The mole fraction of A in the solution is:

(a) 0.5 (b) 0.2 (c) 0.1 (d) 0.8

[Ans. (d)]

[Hint: $p = p^0 x_A$

$32 = 40 \times x_A$ or $x_A = 0.8$]

15. 100 mL of liquid A and 25 mL of liquid B are mixed to form a solution of volume 125 mL. Then the solution is:

(a) ideal

(b) non-ideal with positive deviation

(c) non-ideal with negative deviation

(d) cannot be predicted

[Ans. (a)]

[Hint: $\Delta V_{\text{mix}} = 0$, hence the solution is ideal.]

16. The vapour pressure of pure benzene at 88°C is 957 mm and that of toluene at the same temperature is 379.5 mm. Calculate the composition of benzene-toluene mixture boiling at 88°C:

(a) $x_{\text{benzene}} = 0.66$; $x_{\text{toluene}} = 0.34$

(b) $x_{\text{benzene}} = 0.34$; $x_{\text{toluene}} = 0.66$

(c) $x_{\text{benzene}} = x_{\text{toluene}} = 0.5$

(d) $x_{\text{benzene}} = 0.75$; $x_{\text{toluene}} = 0.25$

[Ans. (a)]

[Hint: $p = p^0_{\text{benzene}}\, x_{\text{benzene}} + p^0_{\text{toluene}}\, x_{\text{toluene}}$

$$760 = 957 \cdot x_{\text{benzene}} + 379.5(1 - x_{\text{benzene}})$$

$$x_{\text{benzene}} = 0.66$$

and $x_{\text{toluene}} = 1 - 0.66 = 0.34$]

17. At 25°C, the total pressure of an ideal solution obtained by mixing 3 mole of A and 2 mole of B, is 184 torr. What is the vapour pressure (in torr) of pure B at the same temperature (Vapour pressure of pure A at 25°C is 200 torr.)? **[CET (J&K) 2006]**

(a) 180 (b) 160 (c) 16 (d) 100

[Ans. (b)]

[Hint: $x_A = \dfrac{n_A}{n_A + n_B} = \dfrac{3}{3+2} = \dfrac{3}{5} = 0.6$

$$x_B = 0.4$$

$$p = p^0_A x_A + p^0_B x_B$$

$$184 = 200 \times 0.6 + p^0_B \times 0.4$$

$$184 = 120 + p^0_B \times 0.4$$

$$p^0_B = \frac{64}{0.4} = 160 \text{ torr}]$$

18. The mass of glucose that would be dissolved in 50 g of water in order to produce the same lowering of vapour pressure as is produced by dissolving 1 g of urea in the same quantity of water is: **(KCET 2006)**

(a) 1 g (b) 3 g (c) 6 g (d) 18 g

[Ans. (b)]

[Hint: $(\Delta p)_{\text{glucose}} = (\Delta p)_{\text{urea}}$

$$(x_B)_{\text{glucose}} = (x_B)_{\text{urea}}$$

i.e., $\left(\dfrac{n_B}{n_A}\right)_{\text{glucose}} = \left(\dfrac{n_B}{n_A}\right)_{\text{urea}}$

$$\frac{w_B}{50} \times \frac{18}{180} = \frac{1 \times 18}{50 \times 60}$$

$$w_B = 3 \text{ g}]$$

5.7 THEORY OF FRACTIONAL DISTILLATION

The process of separation of one liquid from another liquid (binary mixture) having different boiling points by distillation is termed fractional distillation. The information, whether a particular solution of two liquids can be separated by distillation or not, is provided by the study of liquid-vapour equilibrium diagrams at constant pressure, say atmospheric pressure. **The separation is possible only when the vapour phase has a composition different from that of the boiling liquid mixture.**

Liquid pairs of type-I (Ideal solutions): The boiling temperature composition curves for liquid and vapour phases in the case of binary solutions of first type are represented in Fig. 5.4.

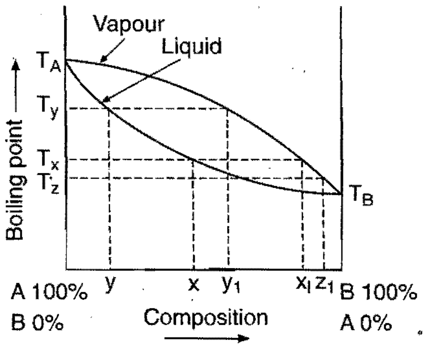


Fig. 5.4 Liquid-vapour equilibrium diagram of a solution of type-I

Suppose a solution of composition x is heated. When the temperature T_x is reached, the boiling will start. At this temperature, the vapour coming off from x will have the composition x_1. Since, x_1 is richer in B than x, the composition of the residual liquid will become richer in A. Let the new composition be y. This liquid cannot boil at temperature T_x but will require higher temperature T_y. The vapour coming off at temperature T_y will also be richer in B as represented by y_1. Hence, the composition of the residue will again be enriched in A. Thus, if the process is allowed to continue, the boiling point of solution will go on increasing towards T_A, the boiling point of pure liquid A. At the same time the solution becomes more and more rich in A. If the process is continued for a sufficiently long time, pure liquid A can be obtained.

Now, if the initial vapours are condensed, the solution obtained will have the composition x_1 and boils at temperature T_z. Evidently, the distillate is richer in B than before. If the process of condensation and redistilling is continued, the final distillate will be pure B component.

Thus, the two liquids forming a solution of type-I can be separated by fractional distillation.

Solution of type-II (Positive deviations from Raoult's law): The boiling temperature-composition curves for the liquid and vapour phases have been shown in Fig. 5.5. The two curves meet at a minimum point C where the liquid and vapour phases have the same composition. The liquid mixture at point C will boil at constant temperature T without undergoing any

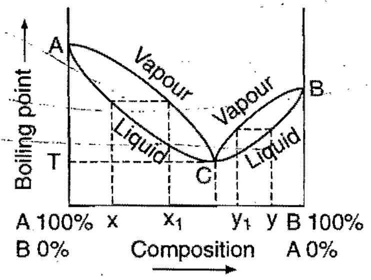


Fig. 5.5 Boiling point-composition curves in binary solution of type-II

change in composition. **Such a mixture which boils at constant temperature and distils over completely at the same temperature without any change in composition, is called constant boiling mixture or azeotropic mixture.**

Consider the distillation of a mixture of composition x. The vapour given off has the composition x_1. The composition of residual liquid will shift towards A. In the mean time the composition of the distillate shifts towards C. Ultimately by repeated fractional distillation, the mixture of composition C will be obtained as distillate and pure liquid A will be left as residue. It will never be possible to have pure B.

When a mixture of composition y is distilled, the vapour given off has the composition y_1, *i.e.*, the composition of residual liquid will shift towards B. Ultimately the mixture of composition C will be obtained as distillate and pure liquid B will be left as residue. It will never be possible to have pure A.

There are several liquid pairs which form minimum boiling point azeotropes. Some examples are given in the table:

Table 5.3 Some Azeotropic Mixtures

	Mixture	% Composition of azeotrope	Boiling point (pressure = 1 atm)
1.	Water-Ethanol	95.97 Ethanol	78.15°C
2.	Pyridine-Water	57.00 Pyridine	92.60°C
3.	Ethanol-Benzene	32.40 Ethanol	67.80°C
4.	Acetic acid-Toluene	28.00 Acetic acid	105.40°C

Solutions of type-III (Negative deviations from Raoult's law): The boiling temperature-composition curves for the liquid and vapour phases have been shown in Fig. 5.6. The curves meet at point C. At this point, both liquid and vapour phases have same composition. The constant-boiling mixture has maximum boiling point.

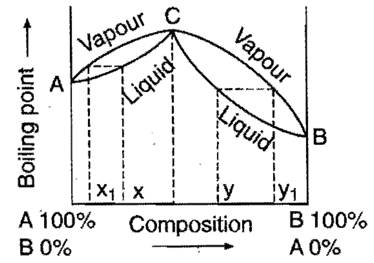


Fig. 5.6 Boiling temperature–composition curves in binary solution of type-III

Consider the distillation of a mixture of composition x. The vapour coming off is richer in A as indicated by composition x_1. The composition of the residual liquid shifts towards C. As the distillation proceeds, the composition of the distillate moves towards A and that of residue towards C.

Similarly, a mixture of composition lying between B and C, say y, on distillation will give vapour richer in B as indicated by composition y_1. The composition of residual liquid shifts towards C and distillate towards A on repeated distillation.

It is never possible to separate a mixture completely into the pure components A and B. It mainly gives a constant boiling mixture (azeotropes) which can never be separated by distillation.

There are several liquid pairs which form maximum boiling point azeotrope. Some examples are tabulated below:

	Mixture	% Composition of azeotrope	Boiling point (pressure = 1 atm)
1.	Nitric acid-Water	68% Nitric acid	125.5°C
2.	Acetic acid-Pyridine	65% Pyridine	139.0°C
3.	Chloroform-Acetone	80% Chloroform	65.0°C
4.	Hydrogen chloride-Water	79.8% Water	108.6°C

5.8 SOLUTIONS OF SOLIDS IN LIQUIDS

Solutions of this type are most common. In solutions of solids in liquids, the liquid is invariably referred to as a solvent and the solid dissolved in it as the solute. If a solute is added in small amounts at a time to a given amount of a solvent at a constant temperature, with vigorous stirring of the solvent after each addition, a stage is reached when the added solute no more disappears, *i.e.*, goes into solution but remains undissolved. The solution is then said to be saturated. **A solution which remains in contact with undissolved solute is termed as saturated.** It can also be defined as **one which is in equilibrium with the excess of solid at a particular temperature.**

The amount of solute dissolved in 100 g of a solvent to form a saturated solution at a given temperature is termed the **solubility** of the solute in the given solvent at that temperature. Each substance has a characteristic solubility in a given solvent at a definite temperature.

When a solid is added to the solvent, the particles from the solid diffuse into it. The solute and solvent molecules move constantly in the solution phase. Some of the particles of the solute return to the solid state due to collisions. Thus, two opposite processes operate simultaneously.

(a) *Dissolution*: Particles of solute leaving the solid and dissolving in the solvent.

(b) *Recrystallisation*: Solute particles returning to the solid form.

When these two processes move with same speed, an equilibrium stage is reached,

$$\text{Solute (solid)} \rightleftharpoons \text{Solute (dissolved)}$$

Thus, a dynamic equilibrium exists in a saturated solution.

When a saturated solution prepared at a higher temperature is cooled, it gives a solution which contains usually more of solute than required for the saturated solution at that temperature. Such a solution is referred to as a **supersaturated solution.** It is usually unstable and changes to saturated solution when excess of solute comes out in solid state.

The following factors influence the solubility of a solute in a liquid:

(1) Nature of solute,
(2) Nature of solvent,
(3) Temperature.

1. Nature of solute: The solutes (solids) can be classified as ionic and non-ionic solids. The ionic solids consist of positively and negatively charged ions. It is the force of attraction between the ions, *i.e.*, lattice energy which opposes the tendency of a solute to dissolve. This force of attraction is different in different ionic solids depending on the charges present on the ions and distance between ions (ionic radii). The ionic solutes having high lattice energy like $BaSO_4$ are less soluble while those having less lattice energy have more solubility. The ions are solvated by the solvent molecules and in this process energy (known as hydration energy) is released. When the hydration energy is high, the ionic solid is more soluble.

Many non-ionic substances dissolve in polar solvents due to hydrogen bonding. Generally, if the solute and solvent have similar characteristics, *i.e.*, both are polar or both non-polar, the solubility is high and if both are dissimilar, the solubility is found low.

2. Nature of solvent: Ionic solids dissolve to a larger extent in a solvent having a high dielectric constant as compared to solvents of low dielectric constants. Dielectric constant of water is 80 while that of methyl alcohol is 33.5. An ionic solid, therefore, dissolves more readily in water than in methyl alcohol. Benzene has a very low dielectric constant of 2.3 and, hence, ionic solids do not dissolve in benzene.

For non-ionic solids, the guiding principle is *'like dissolves like'*, *i.e.*, if the solvent is polar, it will dissolve the polar solutes and if it is non-polar, it will dissolve the non-polar solutes in it.

3. Temperature: The solubility of a solute in a given solvent varies appreciably with temperature. A few curves drawn between solubility in water and temperature are given in Fig. 5.7.

It is observed that the solubility of NaCl increases very slightly with an increase in temperature whereas those of $KNO_3, NaNO_3, AgNO_3$ and KI, etc., increase greatly. A sharp break in a solubility curve indicates the formation of a compound whose solubility is different from that of the substance from which it has been formed as in the case of $Na_2SO_4 \cdot 10H_2O$. It losses its water of crystallisation at 32.3°C and is converted into anhydrous form. There are few substances like calcium acetate, cerium sulphate, calcium chromate, etc., which show a decrease in solubility with rise in temperature.

Generally, solubility depends on heat of solution. **If a substance dissolves with absorption of heat, the solubility increases with rise of temperature.** On the other hand, **if a substance dissolves with evolution of heat, the solubility decreases with rise of temperature.**

Determination of solubility: The solubility of salts is generally determined by gravimetric method. First of all a saturated solution is prepared. Some part of this saturated solution is weighed out in a porcelain dish. The solution is evaporated slowly to dryness on a sand bath. The dish is cooled and weighed again. The observations are recorded as follows:

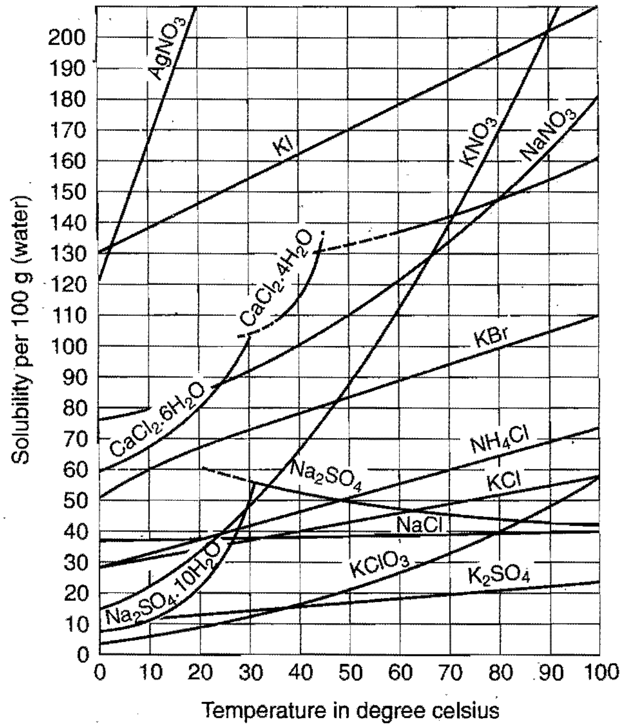


Fig. 5.7 Solubility curves of some compounds

1. Mass of empty dish = w g
2. Mass of dish + solution = w_1 g
3. So, Mass of solution = $(w_1 - w)$ g
4. Mass of dish + residue = w_2 g

So, Mass of residue = $(w_2 - w)$ g = x g

and Mass of solvent = (Mass of solution − Mass of residue)

$$= (w_1 - w) - (w_2 - w)$$
$$= (w_1 - w_2) = y \text{ g}$$

Thus, the solubility of salt $= \frac{x}{y} \times 100$ g per 100 g of solvent.

Example 23: *50 g of a saturated aqueous solution of potassium chloride at* 30°C *is evaporated to dryness, when* 13.2 g *of dry KCl was obtained. Calculate the solubility of KCl in water at* 30°C.

Solution: Mass of water in solution = (50 − 13.2) = 36.8 g

$$\text{Solubility of KCl} = \frac{\text{Mass of KCl}}{\text{Mass of water}} \times 100 = \frac{13.2}{36.8} \times 100 = 35.87 \text{ g}$$

Example 24. *How much copper sulphate will be required to saturate* 100 *g of a dilute aqueous solution of* $CuSO_4$ *at* 25° C *if* 10 *g of the dilute solution leave on evaporation and drying* 1.2 *g of anhydrous* $CuSO_4$? *The solubility of* $CuSO_4$ *in water at* 25° C *is* 25.

Solution: 100 g of dilute solution of $CuSO_4$ contain

$$= 1.2 \times 10 = 12.0 \text{ g } CuSO_4$$

Mass of water present in dilute solution

$$= (100 - 12) = 88 \text{ g}$$

To saturate 100 g of water, $CuSO_4$ required = 25 g

So, to saturate 88 g of water, $CuSO_4$ required $= \frac{25}{100} \times 88$

$= 22\,g$

Thus, the mass of $CuSO_4$ to be added to 100 g of dilute solution to saturate it $= (22 - 12) = 10\,g$

5.9 COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent. The dilute solutions show more or less ideal behaviour as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions obey Raoult's law.

Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as **colligative properties.** The colligative properties are:

(i) Lowering in the vapour pressure,
(ii) Elevation in the boiling point,
(iii) Depression in the freezing point and
(iv) Osmotic pressure.

Colligative properties are the properties of dilute solutions, that is why these are termed as *colligative properties of dilute solutions.* These properties are related to one another. Thus, if one is measured, the other can be calculated. The importance of these properties lies in the fact that they provide methods for the determination of molecular masses of dissolved solutes. The results are excellent if the following three conditions are satisfied:

(i) The solution should be very dilute.
(ii) The solute should be non-volatile.
(iii) The solute does not dissociate or associate in solution.

5.10 LOWERING IN THE VAPOUR PRESSURE

When a non-volatile solute is added to a solvent, the vapour pressure is lowered due to the following reasons:

(i) Percentage surface area occupied by the solvent decreases. Thus, the rate of evaporation and vapour pressure decreases. The solute molecules occupy the surface, and so the per cent surface area occupied by the solvent decreases.

(ii) According to Graham's ~~law of evaporation~~,

$$\text{Rate of evaporation} \propto \frac{1}{\sqrt{\text{density}}}$$

When a non-volatile solute is dissolved in a liquid, its density increases. Thus, both rate of evaporation and vapour pressure are lowered.

If p_0 is the vapour pressure of pure solvent and p_s is the vapour pressure of the solution, the difference $(p_0 - p_s)$ is termed **lowering in vapour pressure** and the ratio $\left[\frac{p_0 - p_s}{p_0}\right]$ is termed **relative lowering in vapour pressure.**

Raoult, in 1886, established a relationship between relative lowering in vapour pressure and composition of the solution after a series of experiments in various solvents. The relationship is known as **Raoult's law.** It states that **the relative lowering in vapour pressure of a dilute solution is equal to mole fraction of the solute present in the solution.**

If n moles of solute be dissolved in N moles of the solvent, the mole fraction of the solute will be $\frac{n}{n+N}$.

According to Raoult's law, $\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$

This is the mathematical expression for Raoult's law.

[**Modified form of Raoult's law:** The above relationship can be written as,

$$\frac{p_0}{p_0 - p_s} = \frac{n+N}{n} = 1 + \frac{N}{n}$$

or $$\frac{p_0}{p_0 - p_s} - 1 = \frac{N}{n} \text{ or } \frac{p_s}{p_0 - p_s} = \frac{N}{n}$$

or $$\frac{p_0 - p_s}{p_s} = \frac{n}{N} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

This equation gives accurate results and is easy to apply.]

Derivation of Raoult's Law for a Dilute Solution

When a non-volatile solute is dissolved in a volatile solvent, a fraction of the surface of solvent is blocked by solute molecules where no evaporation occurs. Thus, under similar conditions, the vapour pressure is decreased. The vapour pressure of the solution, thus, depends upon the number of molecules of the solvent present on the surface of the solution. The number of such molecules is proportional to mole fraction of the solvent.

So, the vapour pressure of solution,

$$`p_s' \propto \frac{N}{n+N}$$

or $$p_s = k \cdot \frac{N}{n+N} \quad \text{... (i)}$$

(k is proportionality factor)

For pure solvent, $n = 0$

and hence, $$p_0 = k \frac{N}{0+N} = k \quad \text{... (ii)}$$

Putting the value of k in eq. (i)

$$p_s = p_0 \frac{N}{n+N}$$

Note : Isopiestic solutions : Two solutions having same vapour pressure at same temperature are known as **isopiestic** solutions.

or $$\frac{p_s}{p_0}=\frac{N}{n+N}$$

or $$1-\frac{p_s}{p_0}=1-\frac{N}{n+N}$$

or $$\frac{p_0-p_s}{p_0}=\frac{n}{n+N} \quad \text{... (iii)}$$

This is Raoult's equation.

If a solution is made by dissolving w_B g of solute (molecular mass m_B) in w_A g of the solvent (molecular mass m_A), the mole fraction of the solute will be

$$\frac{\frac{w_B}{m_B}}{\frac{w_A}{m_A}+\frac{w_B}{m_B}}$$

If the solution is very dilute, $\frac{w_B}{m_B}$ can be neglected in the denominator as compared to $\frac{w_A}{m_A}$. The eq. (iii), thus, becomes

$$\frac{p_0-p_s}{p_0}=\frac{w_B \times m_A}{m_B \times w_A} \quad \text{... (iv)}$$

This relationship is useful in the determination of the molecular mass of dissolved solute by measuring relative lowering of vapour pressure.

Measurement of Relative Lowering in Vapour Pressure (Ostwald and Walker Method)

The apparatus used is shown in Fig. 5.8. It consists of two sets of bulbs. The first set of three bulbs is filled with solution to half of their capacity and second set of another three bulbs is filled with the pure solvent. Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents like P_2O_5, conc. H_2SO_4 etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

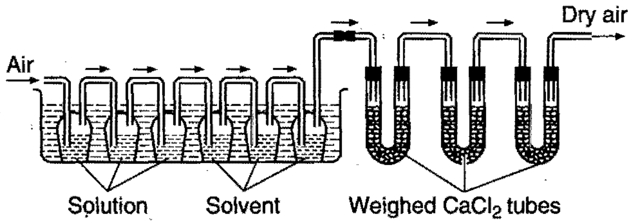


Fig. 5.8 Ostwald and Walker method

A current of pure dry air is bubbled through the series of bulbs as shown in Fig. 5.8. The air gets saturated with the vapours in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution, *i.e.*, $p_0 - p_s$. The two sets of bulbs are weighed again. The guard tubes are also weighed.

Loss in mass in the solution bulbs $\propto p_s$

Loss in mass in the solvent bulbs $\propto (p_0 - p_s)$

Total loss in both sets of bulbs $\propto [p_s + (p_0 - p_s)]$

$\propto p_0$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

Thus, $$\frac{p_0-p_s}{p_0}=\frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}}$$
$$=\frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$$

Further, we know from Raoult's law,

$$\frac{p_0-p_s}{p_0}=\frac{w_B/m_B}{w_A/m_A+w_B/m_B}$$

$$\therefore \quad \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of guard tubes}}=\frac{w_B/m_B}{w_A/m_A+w_B/m_B}$$

The above relationship is used for calculation of molecular masses of non-volatile solutes.

For very dilute solutions, the following relationship can be applied:

$$\frac{p_0-p_s}{p_0}=\frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of guard tubes}}=\frac{w_B \times m_A}{m_B \times w_A}$$

Vapour Pressure of Liquid and Temperature

$$\text{Liquid} \rightleftharpoons \text{Vapour} \qquad \Delta H_{\text{vap.}} > 0$$

Vapour pressure of liquid increases with temperature. Here, ΔH is enthalpy of vaporisation. A graphical representation of vapour pressure *versus* temperature is given below :

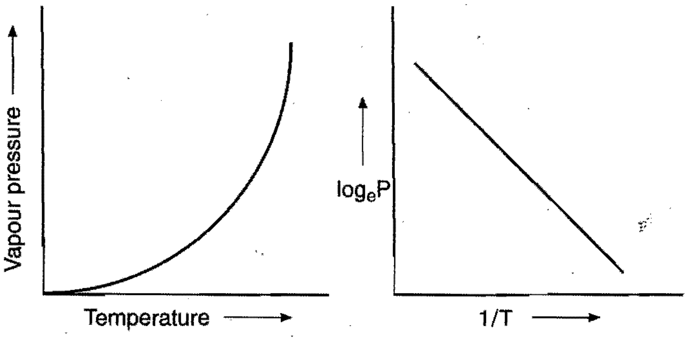


Fig. 5.9 Variation of vapour pressure with temperature

If vapour pressure of a liquid is known at a temperature; it can be calculated at another temperature using Clausius-Clapeyron equation :

$$\log_{10}\left(\frac{P_2}{P_1}\right)=\frac{\Delta H_{\text{vap.}}}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

Here, P_1 = Vapour pressure at temperature T_1

P_2 = Vapour pressure at temperature T_2

SOME SOLVED EXAMPLES

Example 25. *Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.*

Solution: According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$$

or

$$\Delta p = \frac{n}{n+N} \cdot p_0$$

Given: $n = \frac{50}{342} = 0.146$; $N = \frac{500}{18} = 27.78$ and $p_0 = 23.8$

Substituting the values in the above equation,

$$\Delta p = \frac{0.146}{0.146 + 27.78} \times 23.8 = 0.124 \text{ mm Hg}$$

Example 26. *The vapour pressure of pure benzene at a certain temperature is* 640 *mm Hg. A non-volatile solid weighing* 2.175 *g is added to* 39.0 *g of benzene. The vapour pressure of the solution is* 600 *mm Hg. What is the molecular mass of the solid substance?* **(IIT 1990; MLNR 1992)**

Solution: According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$$

Let m be the molecular mass of the solid substance.

$$n = \frac{2.175}{m};\ N = \frac{39}{78} = 0.5$$

(molecular mass of benzene = 78)

$$p_0 = 640 \text{ mm};\ p_s = 600 \text{ mm}$$

Substituting the values in above equation,

$$\frac{640 - 600}{640} = \frac{\frac{2.175}{m}}{\frac{2.175}{m} + 0.5} = \frac{2.175}{2.175 + 0.5\,m}$$

$$m = \frac{2.175 \times 16 - 2.175}{0.5} = 65.25$$

Example 27. *A solution containing* 30 *g of a non-volatile solute in exactly* 90 *g of water has a vapour pressure of* 21.85 *mm of Hg at* 25°*C. Further,* 18 *g of water is then added to the solution; the new vapour pressure becomes* 22.15 *mm of Hg at* 25°*C. Calculate* (*a*) *molecular mass of the solute and* (*b*) *vapour pressure of water at* 25°*C.* **(MLNR 1990)**

Solution: Let the vapour pressure of water at 25°C be p_0 and molecular mass of the solute be m.

Using Raoult's law in the following form,

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm}$$

For solution (I), $\frac{(p_0 - 21.85)}{21.85} = \frac{30 \times 18}{90 \times m}$ ... (i)

For solution (II), $\frac{(p_0 - 22.15)}{22.15} = \frac{30 \times 18}{108 \times m}$ ... (ii)

Dividing eq. (i) by eq. (ii),

$$\frac{(p_0 - 21.85)}{21.85} \times \frac{22.15}{(p_0 - 22.15)} = \frac{108}{90} = \frac{6}{5}$$

$$p_0 = 23.87 \text{ mm of Hg}$$

Substituting the value of p_0 in eq. (i)

$$m = 67.9$$

Example 28. *What mass of non-volatile solute* (*urea*) *needs to be dissolved in* 100 *g of water in order to decrease the vapour pressure of water by* 25%. *What will be the molality of solution?* **(IIT 1993)**

Solution: Using Raoult's law in the following form,

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm},$$

If $p_0 = 100$ mm, then $p_s = 75$ mm

$$\frac{100 - 75}{75} = \frac{w \times 18}{100 \times 60}$$

$$w = 111.1$$

$$\text{Molality} = \frac{w \times 1000}{m \times W} = \frac{111.1 \times 1000}{60 \times 100} = 18.52\,m$$

Example 29. *A current of dry air was bubbled through a bulb containing* 26.66 *g of an organic compound in* 200 *g of water, then through a bulb at the same temperature, containing water and finally through a tube containing anhydrous calcium chloride. The loss of mass in bulb containing water was* 0.087 *g and gain in mass of the calcium chloride tube was* 2.036 *g. Calculate the molecular mass of the organic substance.*

Solution: $\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass of solvent bulb}}{\text{Gain in mass of CaCl}_2 \text{ tube}}$

$$= \frac{0.087}{2.036}$$

Let the molecular mass of the organic substance be m. According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}}$$

$$\frac{0.087}{2.036} = \frac{\frac{26.66}{m}}{\frac{26.66}{m} + \frac{200}{18}} = \frac{26.66}{26.66 + \frac{200}{18}m}$$

$$m = 53.75$$

Example 30. *The vapour pressure of a dilute aqueous solution of glucose is* 750 *mm Hg at* 373 *K. Calculate* (i) *molality,* (ii) *mole fraction of the solute.*

Solution: p_0 = Vapour pressure of water at 373 K = 760 mm Hg

Using Raoult's law in the following form,

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm}$$

or

$$\frac{760 - 750}{750} = \frac{w}{Wm} \times 18$$

or

$$\frac{w}{W \times m} = \frac{10}{750 \times 18}$$

$$\text{Molality} = \frac{w}{W \times m} \times 1000 = \frac{10 \times 1000}{750 \times 18} = 0.74\ m$$

$$p_s = \text{Mole fraction of solvent} \times p_0;$$

$$\text{Mole fraction of solvent} = \frac{750}{760}$$

So, $$\text{Mole fraction of solute} = \left(1 - \frac{750}{760}\right) = 0.0132$$

Example 31. *Calculate the vapour pressure of an aqueous solution which contains 5 mass per cent of urea. The vapour pressure of pure water is 23.5 mm Hg. Molar mass of urea is 60.*

Solution: Mass of urea = 5 g

Mass of water = (100 − 5) = 95 g

$$\text{No. of moles of urea} = \frac{5}{60} = 0.083$$

$$\text{No. of moles of water} = \frac{95}{18} = 5.278$$

$$\text{Total number of moles} = 5.278 + 0.083 = 5.361$$

$$\text{Mole fraction of solvent} = \frac{5.278}{5.361}$$

$$p_s = \text{Mole fraction of solvent} \times p_0 = \frac{5.278}{5.361} \times 23.5 = 23.14 \text{ mm}$$

Example 32. *10 g of glucose (molar mass 180) and 20 g of sucrose (molar mass 342) are dissolved in 100 g of water. What will be the vapour pressure of the resultant solution if the vapour pressure of water is 35 mm Hg?*

Solution: Mass of glucose = 10 g

No. of moles of glucose = 0.0556

Mass of sucrose = 20 g

No. of moles of sucrose = 0.0585

Mass of water = 100 g

No. of moles of water = 5.556

Total number of moles = 5.556 + 0.0585 + 0.0556 = 5.67

$$\text{Mole fraction of water} = \frac{5.556}{5.67}$$

$$\text{Vapour pressure of solution} = \text{Mole fraction of water} \times p_0 = \frac{5.556}{5.67} \times 35 = 34.3 \text{ mm Hg}$$

Example 33. *Calculate the vapour pressure of an aqueous solution of 1.0 molal glucose solution at 100°C.*

Solution: $$\text{Molality} = \frac{w}{m \times W} \times 1000$$

where, w = mass of solute in grams;
W = mass of solvent in grams

$$1.0 = \frac{w}{m \times W} \times 1000$$

or $$\frac{w}{m \times W} = \frac{1.0}{1000} = 0.001$$

Applying Raoult's law for dilute solution,

$$\frac{p_0 - p_s}{p_0} = \frac{w}{m \times W} \times M \qquad (M = 18)$$

$$\frac{760 - p_s}{760} = 0.001 \times 18 \quad (p_0 = 760 \text{ mm at } 100°\text{C})$$

or $$p_s = 760 - 760 \times 0.001 \times 18 = 760 - 13.68 = 746.32 \text{ mm}$$

Example 34. *The vapour pressure of pure benzene at 50°C is 268 mm of Hg. How many moles of non-volatile solute per mole of benzene are required to prepare a solution of benzene having a vapour pressure 167 mm of Hg at 50°C?*

Solution: Applying Raoult's law in the following form:

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm} = \frac{w/m}{W/M}$$

= No. of moles of solute per mole of benzene

or $$\frac{n}{N} = \frac{(268 - 167)}{167} = 0.6047 \approx 0.605$$

Alternative method: We know that, p_s = Mole fraction of solvent × p_0

or 167 = Mole fraction of solvent × 268

So, $$\text{Mole fraction of solvent} = \frac{167}{268} = 0.623$$

Mole fraction of solute = 1 − 0.623 = 0.377

$$\frac{n}{N} = \frac{\text{Mole fraction of solute}}{\text{Mole fraction of solvent}} = \frac{0.377}{0.623} = 0.605$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. The vapour pressure of water at 23°C is 19.8 mm. 0.1 mole glucose is dissolved in 178.2 g of water. What is the vapour pressure (in mm) of the resultant solution?

(a) 19 (b) 19.602 (c) 19.402 (d) 19.202

[Ans. (b)]

[Hint: $n_B = 0.1,\ n_A = \frac{178.2}{18} = 9.9$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{9.9}{9.9 + 0.1} = 0.99$$

$$p = p_0 x_A = 19.8 \times 0.99 = 19.602 \text{ mm}]$$

20. What is the vapour pressure of the solution containing 34.2 g of sucrose per 100 g of water at 25°C? The vapour pressure of water at 25°C is 23.75 mm.

(a) 20.3 mm (b) 23.10 mm

(c) unpredictable (d) 23.33 mm

[**Ans.** (d)]

[**Hint:** $n_A = \frac{w_A}{m_A} = \frac{100}{18} = 5.55$

$$n_B = \frac{34.2}{342} = 0.1$$

$$x_A = \frac{5.55}{5.55 + 0.1} = \frac{5.55}{5.65} = 0.982$$

$$p = p_0 x_A$$

$$= 23.75 \times 0.982 = 23.33 \text{ mm}]$$

21. Lowering of vapour pressure due to a solute in 1 molal aqueous solution at 100°C is:

(a) 13.44 mm Hg (b) 14.12 mm Hg

(c) 31.2 mm Hg (d) 35.2 mm Hg

[**Ans.** (a)]

[**Hint:** $m = \frac{x_B \times 1000}{(1 - x_B) m_A}$ x_B = mole fraction of solute

m_A = molar mass of solvent

$$1 = \frac{x_B \times 1000}{(1 - x_B) \times 18}$$

$$x_B = 0.0176$$

$$x_A = 1 - 0.0176 = 0.9824$$

$$p = p_0 x_A$$

$$= 760 \times 0.9824 = 746.62$$

$$\Delta p = p_0 - p = 760 - 746.62$$

$$\approx 13.4]$$

22. The mass of a non-volatile solute (molecular mass = 40) which should be dissolved in 114 g octane to reduce its vapour pressure to 80% will be:

(a) 20 g (b) 30 g (c) 10 g (d) 40 g

[**Ans.** (c)]

[**Hint:** If $p_0 = 100$, then $p = 80$

$$p = p_0 x_A$$

$$80 = 100 \times x_A$$

$$x_A = 0.80$$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{114/114}{114/114 + w_B/40}$$

$$0.8 = \frac{1}{1 + w_B/40}$$

$$1 + \frac{w_B}{40} = \frac{1}{0.8}$$

$$w_B = 10 \text{ g}]$$

23. 3g urea is dissolved in 45g of water. The relative lowering of vapour pressure is : **[Comed (Karnataka) 2008]**

(a) 0.05 (b) 0.04 (c) 0.02 (d) 0.01

[**Ans.** (c)]

[**Hint:** $n_B = \frac{3}{60} = 0.05;$ $n_A = \frac{45}{18} = 2.5$

$$\frac{\Delta p}{p_0} = x_B = \frac{0.05}{2.5 + 0.05} = 0.0196 \approx 0.02\ ]$$

24. When 25g of a non-volatile solute is dissolved in 100g of water, the vapour pressure is lowered by 0.225 mm. If the vapour pressure of water at 25°C is 17.5 mm, what is the molecular mass of the solute ? **[EAMCET (Engg) 2008]**

(a) 206 (b) 302 (c) 318 (d) 276

[**Ans.** (c)]

[**Hint :** $p = p_0 x_A$

$$(17.5 - 0.225) = 17.5 \times \frac{100/18}{100/18 + \frac{25}{m_B}}$$

$$\frac{17.275}{17.5}\left(\frac{100}{18} + \frac{25}{m_B}\right) = \frac{100}{18}$$

$$0.987\left(5.55 + \frac{25}{m_B}\right) = 5.55$$

$$5.55 + \frac{25}{m_B} = 5.628$$

$$m_B \approx 318 \text{ mm}]$$

5.11 ELEVATION OF BOILING POINT (Ebullioscopy)

The boiling point of a liquid is **the temperature at which its vapour pressure is equal to the atmospheric pressure.** The vapour pressure of a liquid is lowered when a non-volatile solute is added to it. Hence, the temperature of the solution when its vapour pressure will be equal to atmospheric pressure will be higher than the temperature of the pure solvent. In other words, the boiling point of the solvent is elevated by the addition of non-volatile solute. The difference in the boiling point of the solution and the boiling point of the pure solvent is termed **elevation of boiling point.**

Elevation of boiling point,

(ΔT) = Boiling point of the solution − Boiling point of pure solvent

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions of different concentrations. The curves of the solutions always lie below the curve of the pure solvent. The line P_0C represents the atmospheric pressure. T_0, T_1 and T_2 represent the boiling points of pure solvent, solution I and solution II respectively. The vapour pressure of pure solvent, solution I and solution II at temperature T_0 are P_0, P_1 and P_2 respectively.

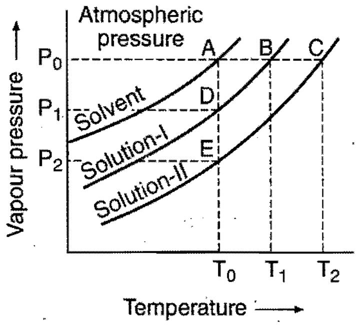


Fig. 5.10

Assuming that the solutions are very dilute, these curves may be approximately taken as straight lines near the boiling point. Thus, ΔACE and ΔABD are similar.

Therefore, $$\frac{AC}{AB} = \frac{AE}{AD}$$

or $$\frac{T_2 - T_0}{T_1 - T_0} = \frac{P_0 - P_2}{P_0 - P_1}$$

or $$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

or $$\Delta T \propto \Delta P$$

From Raoult's law for dilute solution,

$$\frac{p_0 - p_s}{p_0} = \frac{w_B \times m_A}{m_B \times w_A}$$

(p_s = vapour pressure of solution)

or $$p_0 - p_s = \frac{w_B \times m_A}{m_B \times w_A} \cdot p_0$$

For the pure solvent, p_0 (its vapour pressure at the boiling point) and m_A (its molecular mass) are constant. Therefore,

$$p_0 - p_s \propto \frac{w_B}{m_B \times w_A}$$

or $$\Delta p \propto \Delta T \propto \frac{w_B}{m_B \times w_A}$$

or $$\Delta T = K \cdot \frac{w_B}{m_B \times w_A} \qquad \text{... (i)}$$

where K is a constant, called as elevation constant.

When, $\frac{w_B}{m_B} = 1$, (one mole of solute) and $w_A = 1\,\text{g}$, then

$$\Delta T = K$$

Thus, boiling point constant is equal to the elevation in boiling point which would be theoretically produced when 1 mole of a non-volatile solute is dissolved in 1 g of the solvent.

If $\frac{w_B}{m_B} = 1$ and $w_A = 100\,\text{g}$,

Then, $$\Delta T = \frac{K}{100} = K'$$

K' is called **molecular elevation constant.** It is defined as the **elevation in boiling point produced when 1 mole of the solute is dissolved in 100 g of the solvent.**

Thus, $$K = 100K'$$

Putting this value in eq. (i),

$$\Delta T = 100K' \cdot \frac{w_B}{m_B\ w_A} \qquad \text{... (ii)}$$

If $\frac{w_B}{m_B} = 1$ and $w_A = 1000\,\text{g}$,

Then, $$\Delta T = \frac{K}{1000} = K_b$$

K_b is called **molal elevation constant.** It is defined as the **elevation in boiling point produced when 1 mole of the solute is dissolved in 1000 g of the solvent.**

Thus, $$K = 1000\,K_b$$

Putting this value in eq. (i),

$$\Delta T = \frac{1000 K_b\ w_A}{m_A\ w_B} \qquad \text{... (iii)}$$

or $$\Delta T = \text{Molality} \times K_b$$

$$\left(\text{since } \frac{w_B}{m_B \times w_A} \times 1000 = \text{molality}\right)$$

The elevation in boiling point of a solution o non-electrolyte is proportional to its molality and equimolal solutions of all the substances in the same solvent will show equal elevation in boiling points. These are known as Raoult's laws of elevation of boiling point.

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{RT_b^{\,2}}{1000\,L_v}$$

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 vaporisation of solvent in calories per gram.

For water $$K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515$$

The molal elevation constants for some common solvents are given in the following table:

Table 5.4 Molal Elevation Constants of Some Solvents

Solvent	B.pt. (°C)	Molal elevation constant (K kg mol^{-1})
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.67
Carbon tetrachloride	76.8	5.02
Benzene	80.0	2.70
Ethyl alcohol	78.4	1.15

If $K_b, w_A, \Delta T$ and w_B are known, molecular mass of a non-volatile solute can be determined. The most convenient method for the determination of ΔT in the laboratory is the **Landsberger method.**

---

* This relation may also be written as:

$$\Delta T = \frac{1000\,K_b \times w}{m \times W}$$

where, w and W are masses of solute and solvent respectively and m = molecular mass of solute.

5.12 DEPRESSION OF FREEZING POINT (Cryoscopy)

Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid. Since, the addition of a non-volatile solute always lowers the vapour pressure of a solvent, therefore, it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature. The difference between the freezing points of the pure solvent and its solution is called **depression of freezing point.**

Depression of freezing point

$$(\Delta T) = \text{Freezing point of the solvent} - \text{Freezing point of the solution}$$

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions, solution I and solution II. CFB is a curve for a solid solvent. The solvent, solution I and solution II vapour pressure curves meet CFB curve at points B, F and C respectively. Thus, T_0, T_1 and T_2 are the freezing points of pure solvent, solution I and solution II respectively. The vapour pressures at temperatures T_0, T_1 and T_2 for solvent, solution I and solution II are, thus, P_0, P_1 and P_2 respectively.

For very dilute solutions, the curves FD and CE are almost straight lines and CB is also nearly a straight line. The ΔBEC and ΔBDF are similar.

So, $$\frac{EC}{DF} = \frac{BE}{BD}$$

or $$\frac{T_0 - T_2}{T_0 - T_1} = \frac{P_0 - P_2}{P_0 - P_1}$$

or $$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

or $$\Delta T \propto \Delta P$$

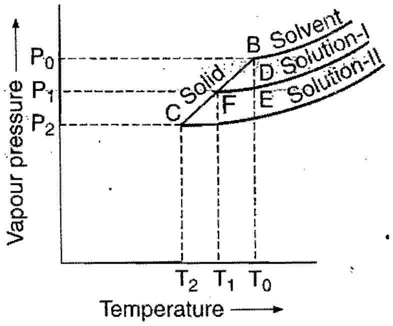


Fig. 5.11

From Raoult's law for dilute solutions,

$$\frac{p_0 - p_s}{p_0} = \frac{w_B}{m_B} \cdot \frac{m_A}{w_A}$$

or $$p_0 - p_s = \frac{w_B}{m_B} \cdot \frac{m_A}{w_A} \cdot p_0$$

For the pure solvent, p_0 and m_B are constants. Therefore,

$$p_0 - p_s \propto \frac{w_B}{m_B\ w_A}$$

or $$\Delta p \propto \frac{w_B}{m_B\ w_A}$$

or $$\Delta p \propto \Delta T \propto \frac{w_B}{m_B\ w_A}$$

or $$\Delta T = K \cdot \frac{w_B}{m_B\ w_A} \qquad \text{... (i)}$$

where, K is a constant, called depression constant.

When, $\frac{w_B}{m_B} = 1$ (one mole of solute) and $w_A = 1\text{g}$

$$\Delta T = K$$

Thus, depression constant is equal to the depression of the freezing point which would be theoretically produced when one mole of a non-volatile solute is dissolved in 1 g of the solvent.

If $\frac{w_B}{m_B} = 1$ and $w_B = 100\text{g}$,

$$\Delta T = \frac{K}{100} = K'$$

K' is called molecular depression constant.

It is defined as the depression of freezing point produced when 1 mole of the solute is dissolved in 100 g of the solvent.

Thus, $K = 100K'$

Putting this value in eq. (i),

$$\Delta T = \frac{100K' \times w_B}{m_B \times w_A} \qquad \text{... (ii)}$$

If $\frac{w_B}{m_B} = 1$ and $w_A = 1000\text{g}$

$$\Delta T = \frac{K}{1000} = K_f$$

K_f is called molal depression constant.

It is defined as the depression of freezing point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

Thus, $K = 1000K_f$

Putting this value in eq. (i),

$$\Delta T = 1000K_f \frac{w_B}{m_B\ w_A} \qquad \text{... (iii)}$$

---

* This relation may also be written as:

$$\Delta T = \frac{1000\ K_f \times w}{m \times W}$$

where w and W are the masses of solute and solvent respectively and m = molecular mass of solute.

or $$\Delta T = \text{molality} \times K_f$$

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

$$K_f = \frac{0.002\,T_f^2}{L_f}$$

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,

$$K_f = \frac{0.002 \times (273)^2}{80}$$

$$= 1.86\,\text{K kg mol}^{-1}$$

The molal depression constants for some common solvents are given in the following table:

Table 5.5 Molal Depression Constants of Some Solvents

Solvent	**F.pt. (°C)**	**Molal elevation constant (K kg mol^{-1})**
Water	0.0	1.86
Ethyl alcohol	−114.6	1.99
Chloroform	−63.5	4.70
Carbon tetrachloride	−22.8	29.80
Benzene	5.5	5.12
Camphor	179.0	39.70

If $K_f, w_A, \Delta T$ and w_B are known, molecular mass of a non-volatile solute can be determined. ΔT is measured by Beckmann's method in the laboratory.

The molecular mass of non-volatile and non-ionisable solute can be calculated using following formula:

$$m_B = \frac{K_f}{\Delta T} \times \frac{w_B}{w_A} \times 1000$$

where, w_B and w_A are the masses of solute and solvent respectively.

Anti-freeze solutions : Water is used in radiators of cars and other automobiles. In cold countries where the atmospheric temperature becomes less than zero degree, the water in the radiators would freeze. Anti-freeze solutions are useful under these conditions when the vehicles are used in the regions of sub-zero temperature so that the water does not freeze in radiators. Such solutions are made by dissolving ethylene glycol in water. Freezing point can be lowered to the desired extent by varying the concentration of ethylene glycol. Glycerol can also be used as anti-freeze.

Freezing mixture : It is a mixture of ice and common salt (NaCl). It is used in the making of ice-cream and in the laboratories to create low temperatures. With the help of this mixture, a temperature as low as −33°C (240 K) can be achieved.

Note: Ebullioscopic and cryoscopic methods are effective when :

(i) Solutions are dilute. Solutions obey Raoult's law.
(ii) The solute is non-volatile.
(iii) There is no association or dissociation of solute molecules in the solution.
(iv) Solute does not form a solid solution with solvent in frozen state, *i.e.*, only solvent separates in solid state on freezing the solution.
(v) Equimolal quantities of different substances dissolved in the same quantity of solvent bring out the same depression in freezing point of the solvent under identical conditions.

SOME SOLVED EXAMPLES

Example 35. *On dissolving* 10.8 g *glucose* (*m.wt.* = 180) *in* 240 g *of water, its boiling point increases by* 0.13° C. *Calculate the molecular elevation constant of water.*

Solution: $$\Delta T = \frac{100K' \times w}{W \times m}$$

or $$K' = \frac{\Delta T \times W \times m}{100 \times w}$$

Given, $\Delta T = 0.13°$ C, $W = 240$ g, $m = 180$ and $w = 10.8$ g

$$K' = \frac{0.13 \times 240 \times 180}{100 \times 10.8} = 5.2°.$$

Example 36. *A solution of* 2.5 g *of a non-volatile solid in* 100 g *benzene is boiled at* 0.42°C *higher than the boiling point of pure benzene. Calculate the molecular mass of the substance. Molal elevation constant of benzene is* 2.67 K *kg mol*$^{-1}$.

Solution: $$m = \frac{1000K_b \times w}{W \times \Delta T}$$

Given, $K_b = 2.67$, $w = 2.5\,\text{g}$, $W = 100\,\text{g}$, $\Delta T = 0.42$

$$m = \frac{1000 \times 2.67 \times 2.5}{100 \times 0.42} = 158.9$$

The molecular mass of substance is 158.9.

Example 37. *The molal elevation constant for water is* 0.56 K *kg mol*$^{-1}$. *Calculate the boiling point of a solution made by dissolving* 6.0 g *of urea* (NH_2CONH_2) *in* 200 g *of water.*

Solution: $$\Delta T = \frac{1000K_b \times w}{m \times W}$$

Given, $K_b = 0.56\,\text{K kg mol}^{-1}$, $w = 6.0\,\text{g}$, $W = 200\,\text{g}$, $m = 60$

$$\Delta T = \frac{1000 \times 0.56 \times 6.0}{200 \times 60} = 0.28°\,\text{C}$$

Thus, the boiling point of solution = b.pt. of water + ΔT

$$= (100°\,\text{C} + 0.28°\,\text{C}) = 100.28°\,\text{C}$$

Example 38. *By dissolving* 13.6 g *of a substance in* 20 g *of water, the freezing point decreased by* 3.7°C. *Calculate the molecular mass of the substance. (Molal depression constant for water* = 1.863 K *kg mol*$^{-1}$)

Solution: $$m = \frac{1000K_f \times w}{W \times \Delta T}$$

Given, $K_f = 1.863\,\text{K kg mol}^{-1}$

$$w = 13.6\,\text{g}, W = 20\,\text{g}, \Delta T = 3.7°\,\text{C}$$

$$m = \frac{1000 \times 1.863 \times 13.6}{20 \times 3.7} = 342.39$$

Example 39. *On dissolving 0.25 g of a non-volatile substance in 30 mL benzene (density 0.8 g / mL), its freezing point decreases by 0.40°C. Calculate the molecular mass of non-volatile substance ($K_f = 5.12\ K\ kg\ mol^{-1}$).*

Solution: Mass of benzene, W = volume × density

$$= 30 \times 0.8 = 24\text{ g}$$

Given, $K_f = 5.12\text{ K kg mol}^{-1}$, $w = 0.25\text{ g}$, $\Delta T = 0.40°\text{C}$.

We know that,

$$m = \frac{1000 K_f \times w}{W \times \Delta T}$$

$$= \frac{1000 \times 5.12 \times 0.25}{24 \times 0.40} = 133.33$$

Example 40. *A solution of 1.25 g of a certain non-volatile substance in 20 g of water freezes at 271.94 K. Calculate the molecular mass of the solute ($K_f = 1.86\ K\ kg\ mol^{-1}$).*

Solution: Freezing point of solution = 271.94 K

Freezing point of water = 273.0 K

$$\Delta T = (273 - 271.94) = 1.06\text{ K}$$

We know that, $$m = \frac{1000 K_f \times w}{W \times \Delta T}$$

Given, $K_f = 1.86\text{ K kg mol}^{-1}$, $w = 1.25$ g, $W = 20$ g and $\Delta T = 1.06$ K.

$$m = \frac{1000 \times 1.86 \times 1.25}{20 \times 1.06} = 109.66$$

Example 41. *Two elements A and B form compounds having molecular formulae AB_2 and AB_4. When dissolved in 20.0 g of benzene, 1.0 g of AB_2 lowers the freezing point by 2.3°C, whereas 1.0 g of AB_4 lowers the freezing point by 1.3° C. The molal depression constant for benzene in 1000 g is 5.1. Calculate the atomic masses of A and B.*

Solution: We know that,

$$m = \frac{1000 K_f \times w}{W \times \Delta T}$$

Molecular mass of AB_2 (from given data) $= \dfrac{1000 \times 5.1 \times 1}{20 \times 2.3}$

$$= 110.86$$

and Molecular mass of AB_4 (from given data) $= \dfrac{1000 \times 5.1 \times 1}{1.3 \times 20}$

$$= 196.15$$

Further, $$AB_4 = A + 4B = 196.15 \quad \text{... (i)}$$

$$AB_2 = A + 2B = 110.86 \quad \text{... (ii)}$$

Subtracting eq. (ii) from (i),

$$2B = 85.29$$

$$B = 42.645$$

Putting the value of B in eq. (ii),

$$A + 85.29 = 110.86$$

or $$A = (110.86 - 85.29) = 25.57$$

Thus, the atomic masses of A and B are 25.57 and 42.645 respectively.

Example 42. *1.355 g of a substance dissolved in 55 g of CH_3COOH produced a depression in the freezing point of 0.618°C. Calculate the molecular weight of the substance ($K_f = 3.85$).* **[CECE (Mains) Bihar 2005]**

Solution: $$\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$$

where, w_B = mass of solute, m_B = molar mass of solute, w_A = mass of solvent

$$0.618 = 3.85 \times \frac{1.355 \times 1000}{m_B \times 55}$$

$$m_B = 153.47$$

Example 43. *An aqueous solution of a non-volatile solute boils at 100.17°C. At what temperature will the solution freeze? (Given: $K_b = 0.512\ K\ kg\ mol^{-1}$ and $K_f = 1.86 K\ kg\ mol^{-1}$)*

Solution: We know that,

$$\Delta T_b = \text{molality} \times K_b$$

$$0.17 = \text{molality} \times 0.512$$

Molality of the solution $= \dfrac{0.17}{0.512}\ m$

Let depression in freezing point be ΔT_f

$$\Delta T_f = \text{molality} \times K_f$$

$$= \frac{0.17}{0.512} \times 1.86 = 0.62°\text{ C}$$

Thus, the freezing point of the solution is

$$0.00 - 0.62 = -0.62°\text{C}$$

Example 44. *18 g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a saucepan. At what temperature will the water boil (1.013 bar pressure)? K_b for water is 0.52 K kg mol^{-1}.*

Solution: $$\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$\Delta T = 0.52 \times \frac{18 \times 1000}{180 \times 1000}$$

$$T - T_0 = 0.052$$

$$T - 373 = 0.052$$

$$T = 373.052\text{ K}$$

Example 45. *A solution of urea in water has boiling point of 100.15°C. Calculate the freezing point of the same solution if K_f and K_b for water are 1.87 K kg mol^{-1} and 0.52 K kg mol^{-1} respectively.*

Solution: $$\Delta T_b = (100.15 - 100) = 0.15°\text{C}$$

We know that, $$\Delta T_b = \text{molality} \times K_b$$

$$\text{Molality} = \frac{\Delta T_b}{K_b} = \frac{0.15}{0.52} = 0.2884$$

$$\Delta T_f = \text{molality} \times K_f$$

$$= 0.2884 \times 1.87 = 0.54° \text{ C}$$

Thus, the freezing point of the solution = – 0.54 °C

Example 46. *In a cold climate, water gets frozen causing damage to radiator of a car. Ethylene glycol is used as antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at* $-6°C$ *(*K_f *for water* = 1.85 *K kg mol* $^{-1}$*).* **(IIT 1992)**

Solution: Given,

$$\Delta T = 6°\text{C},\ W = 4 \text{ kg} = 4000 \text{ g},\ m = 62,\ K_f = 1.85$$

$$w = \frac{m \times W \times \Delta T}{1000 \times K_f}$$

$$= \frac{62 \times 4000 \times 6}{1000 \times 1.85} = 804.32 \text{ g}$$

Example 47. *A solution containing* 0.2563 *g of naphthalene (molecular mass* = 128*) in* 50 *g of carbon tetrachloride yields a boiling point elevation of* 0.201°*C while a solution of* 0.6216 *g of an unknown solute in the same mass of the solvent gives a boiling point elevation of* 0.647°*C. Find the molecular mass of the unknown solute.*

Solution: We know that,

$$K_b = \frac{\Delta T_b \times W \times m}{1000 \times w}$$

For CCl_4, $$K_b = \frac{0.201 \times 50 \times 128}{1000 \times 0.2563} = 5.019$$

K_b is now used in the second part of the problem.

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

$$= \frac{1000 \times 5.019 \times 0.6216}{0.647 \times 50} = 96.44$$

Example 48. *Calculate the molal depression constant of a solvent which has freezing point* 16.6°*C and latent heat of fusion* 180.75 *J g*$^{-1}$.

Solution: $$K_f = \frac{RT_f^2}{1000 \times L_f}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$T_f = 16.6° \text{C} = 273 + 16.6 = 289.6 \text{ K},$$

$$L_f = 180.75 \text{ J g}^{-1}.$$

Substituting the values in the above equation,

$$K_f = \frac{8.314 \times (289.6)^2}{1000 \times 180.75} = 3.86$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

25. Calculate the molal depression constant of a solvent which has freezing point 16.6°C and latent heat of fusion 180.75 J g^{-1}: **[JEE (Orissa) 2005]**

(a) 2.68 (b) 3.86 (c) 4.68 (d) 2.86

[**Ans.** (b)]

[**Hint:** $K_f = \dfrac{RT_0^{\ 2}}{1000L}$ $\qquad T_0 = 273 + 16.6 = 289.6$ K

$$= \frac{8.314 \times (289.6)^2}{1000 \times 180.75}$$

$$= 3.86]$$

26. The elevation in boiling point for 13.44 g of $CuCl_2$ dissolved in 1 kg of water as solvent will be (K_b = 0.52 K kg mol^{-1}; molar mass of $CuCl_2$ = 134.4 g/mol): **(IIT 2005)**

(a) 0.05 (b) 0.10 (c) 0.16 (d) 0.20

[**Ans.** (c)]

[**Hint:** $i = 3$, assuming complete ionization of $CuCl_2$

$$\Delta T = i \times K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$= 3 \times 0.52 \times \frac{13.44 \times 1000}{134.4 \times 1000} = 0.156 \approx 0.16]$$

27. A solution containing 7 g of a solute (molar mass 210 g mol^{-1}) in 350 g of acetone raised the boiling point of acetone from 56°C to 56.3°C. The value of ebullioscopic constant of acetone in K kg mol^{-1} is:

(a) 2.66 (b) 3.15 (c) 4.12 (d) 2.86

[**Ans.** (b)]

[**Hint:** $$\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = K_b \times \frac{7 \times 1000}{210 \times 350}$$

$$K_b = \frac{0.3 \times 210 \times 350}{7 \times 1000} = 3.15 \text{ K kg mol}^{-1}]$$

28. The normal boiling point of toluene is 110.7°C and its boiling point elevation constant is 3.32 K kg mol^{-1}. The enthalpy of vaporization of toluene is nearly:

(a) 17 kJ mol^{-1} (b) 21 kJ mol^{-1}

(c) 51 kJ mol^{-1} (d) 68 kJ mol^{-1}

[**Ans.** (b)]

[**Hint:** $K_b = \dfrac{RT_0^{\ 2}}{1000L}$; $3.32 = \dfrac{(8.314 \times 10^{-3}) \times (383.7)^2}{1000 \times L}$

$$L = 0.368 \text{ kJ/g}$$

Latent heat per mol = 0.368 × molar mass of acetone

$$= 0.368 \times 58 = 21.344 \text{ kJ mol}^{-1}]$$

29. An aqueous solution freezes at $-0.186°C$ (K_f = 1.86 K kg mol^{-1}, K_b = 0.512 K kg mol^{-1}). The elevation of b. pt. of the solution is:

(a) 0.186 (b) 0.512 (c) $\frac{0.512}{1.86}$ (d) 0.0512

[**Ans.** (d)]

[**Hint:** $\Delta T = K_f \times m$

$0.186 = 1.86 \times m$

$m = 0.1$

$\Delta T = K_b \times m = 0.512 \times 0.1 = 0.0512$]

30. The amount of urea to be dissolved in 500 cc of water ($K_f = 1.86$) to produce a depression of 0.186°C in the freezing point is: **[UGET (Manipal) 2006]**

(a) 9 g (b) 6 g (c) 3 g (d) 0.3 g

[**Ans.** (c)]

[**Hint:** $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$0.186 = 1.86 \times \frac{w_B \times 1000}{60 \times 500}$

$w_B = 3$ g]

31. What should be the freezing point of aqueous solution containing 17 g of C_2H_5OH in 1000 g of water (K_f for water = 1.86 deg kg mol^{-1})?

(a) − 0.69°C (b) 0.34°C

(c) 0.0°C (d) − 0.34°C

[**Ans.** (a)]

[**Hint:** $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A} = 1.86 \times \frac{17 \times 1000}{46 \times 1000} = 0.69$

∴ Freezing point of solution = 0 − 0.69 = − 0.69°C]

5.13 OSMOSIS AND OSMOTIC PRESSURE

Osmosis: When a semipermeable membrane is placed between a solution and a solvent, it is observed that solvent molecules enter the solution and the volume of solution increases. It is also observed that if two solutions of unequal concentrations are separated by a semipermeable membrane, the solvent molecules from a solution of lower concentration move towards a solution of higher concentration. This phenomenon was first observed by **Abbe Nollet** (1748) and termed as **Osmosis** (Greek, *osmos* = to push). Osmosis is defined **as the spontaneous flow of solvent molecules through semipermeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.**

The phenomenon of osmosis can be demonstrated by the following experiment:

Two eggs of same size are taken and their outer hard shell is removed by dissolving in dilute hydrochloric acid. One of the eggs is placed in distilled water and the other in saturated salt solution.

After sufficient time, it is noticed that the egg placed in water swells up and that placed in salt solution shrinks. In the first case, water enters the concentrated egg fluid while in the second case, water comes out of the egg as salt solution is more concentrated than the egg fluid.

Difference between Osmosis and Diffusion

The two processes, diffusion and osmosis, can be distinguished in terms of the following aspects:

(i) In diffusion, solute as well as solvent molecules flow in opposite directions while in osmosis the flow of solvent molecules occurs in one direction only.

(ii) For osmosis, a semipermeable membrane* is required while for diffusion it is not required.

Semipermeable membrane

"A membrane which allows the solvent molecules to pass through it but prevents the passage of solute molecules through it is called a semipermeable membrane."

Examples of semipermeable membranes are too many. Parchment paper, membranes covering the animal and plant cells and many gelatinous inorganic substances such as calcium phosphate and copper ferrocyanide, etc., act as semipermeable membranes. Animal and plant membranes are not all completely semipermeable. The best semipermeable membrane used is prepared by deposition of copper ferrocyanide, $Cu_2[Fe(CN)_6]$, in the pores of a porous pot.

Working of semipermeable membrane : Several theories have been put forward to explain the working of semipermeable membrane. These are :

(a) The sieve theory : The theory was suggested by Traube. According to this theory, a semipermeable membrane contains a large number of small pores which act like a sieve. The pores allow the smaller molecules of solvent to pass through it but does not allow the larger molecules of solute to do so. However, this theory fails in those cases of semipermeability where the solute molecules are smaller than the solvent molecules.

(b) The solution theory : According to this theory, a membrane is permeable to those substances which dissolve in it and is impermeable to those which are insoluble in it. Thus, a layer of phenol acts as a semipermeable membrane when placed between a solution of $Ca(NO_3)_2$. Phenol allows water to pass through it because water is soluble in phenol. It is impermeable to $Ca(NO_3)_2$ because $Ca(NO_3)_2$ is insoluble in phenol.

(c) Vapour pressure theory : According to this theory, a solvent can pass through a semipermeable membrane because the vapour pressure of the pure solvent is higher than the vapour pressure of the solution. This theory is widely accepted because it explains the phenomenon of osmosis.

Osmotic pressure: A porous pot is taken and a semipermeable membrane of copper ferrocyanide is deposited in its walls. It is fitted with a long glass tube with the help of a rubber stopper. It is filled with concentrated aqueous sugar solution and placed in distilled water. Osmosis occurs and the level of the solution in glass tube rises over a period of time. After a few days, the level becomes stationary. At this equilibrium state the hydrostatic pressure of the liquid column exactly balances the tendency which enables the water molecules to pass through semipermeable membrane.

---

* Membranes which allow the passage of only solvent molecules through them are called semipermeable membranes. Egg membrane, goat's bladder and cell membranes can serve as semipermeable membranes but these are not perfect for laboratory measurements. Artificial membranes of gelatinous inorganic substances such as copper ferrocyanide are used these days as semipermeable membranes.

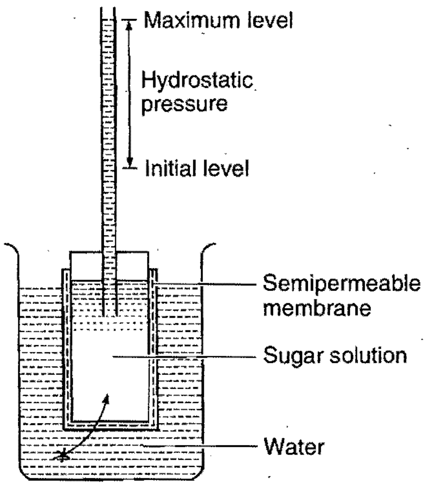


Fig. 5.12 Hydrostatic pressure determination

The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution. Osmotic pressure is also defined **as the hydrostatic pressure built up on the solution which just stops the osmosis.**

Osmotic pressure = hydrostatic pressure

$$\pi = hdg$$

where, h = increase in level in the tube of unit cross section, d = density of solution and g = acceleration due to gravity.

Actually, this will not be an exact measure of osmotic pressure of the solution originally taken because sufficient dilution has taken place with time.

If osmosis takes place due to concentration gradient *i.e.*, when two solutions of different concentration are separated by semipermeable membrane then,

$$\pi = hdg = \Delta CRT$$

Alternative definition: An apparatus as shown in Fig. 5.13 consists of a water-tight chamber which is divided into two halves by a semipermeable membrane and fitted with a water-tight piston and a flow indicator in separate compartments. The compartment having a piston is filled with solution and the other compartment is filled with a pure solvent. Water (solvent) tries to flow into the solution side. To check this tendency, a certain pressure shall have to be applied by the piston. This external pressure is thus a measure of osmotic pressure of the solution. **The external pressure which must be applied on the solution in order to stop the flow of the solvent into the solution through semipermeable membrane is equal to osmotic pressure.**

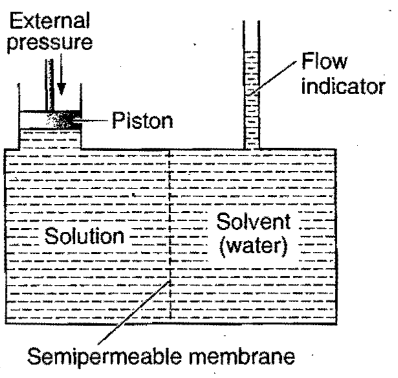


Fig. 5.13

Determination of Osmotic Pressure: Berkeley and Hartley's Method

Various methods are employed for the measurement of osmotic pressure but the best known method was suggested by Berkeley and Hartley. The apparatus used is shown in Fig. 5.14. A porcelain tube having copper ferrocyanide membrane in its walls is enclosed in a metallic jacket. The porcelain tube is fitted with a reservoir of pure solvent at one end and a capillary tube at the other end. In a metallic jacket, there is an arrangement for applying external pressure which is measured with the help of pressure gauge.

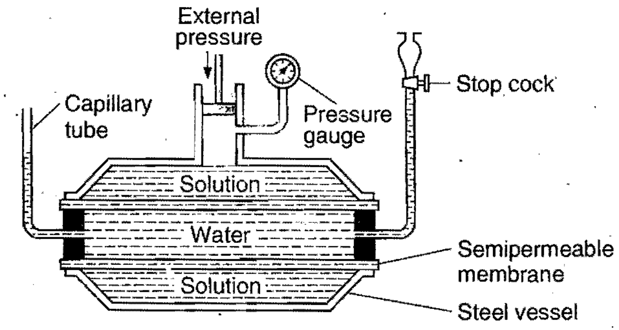


Fig. 5.14 Berkeley and Hartley's method

Procedure: The porcelain tube is filled with pure solvent and the metallic jacket with solution. The level in the capillary tube will tend to move down as the solvent flows towards solution due to osmosis. External pressure is now applied on the solution by the piston so that level in capillary remains stationary. The reading of pressure gauge is recorded. This is the osmotic pressure of the solution.

Advantages: (i) It is a quick and accurate method.

(ii) The concentration of the solution does not change because flow of solvent is not permitted into solution; so the results obtained by this method are reliable.

(iii) As the osmotic pressure is balanced by external pressure, there is no strain on membrane and the danger of its bursting is eliminated. So, this method can be used to measure high osmotic pressures also.

Comparison of osmotic pressures: de-Vries developed an approximate method for comparing the relative osmotic pressures of aqueous solutions. A solution of low osmotic pressure is termed **hypotonic** and solution of high osmotic pressure is termed **hypertonic.** The protoplasmic layer, lining the cell walls of plant cells is easily penetrated by water but is almost impermeable to the substances dissolved in the cellular fluid. When a plant cell is placed in hypotonic solution, the water is drawn in and the cell swells. If the cell is placed in a hypertonic solution, water will diffuse out of the cell fluid and partial collapse of the cell will take place when hypotonic solution is separated from hypertonic solution using semipermeable membrane, then osmosis takes place from hypotonic to hypertonic because solvent concentration is greater in hypotonic solution. This phenomenon is known as **plasmolysis.** The change in cell can be observed under a microscope. When the plant cell is placed in the solution of same osmotic pressure as that of the cell fluid, no change in the structure of the cell is observed. Such solutions having same osmotic pressures are termed **isotonic.** By putting, therefore, cells of the same kind into solutions of different concentrations, it can be ascertained whether the solution is hypertonic or hypotonic or isotonic.

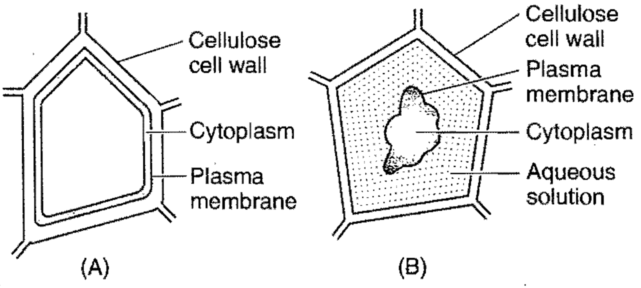


Fig. 5.15 Plasmolysis

Some biological explanation on the basis of osmosis are given below:

(i) In animals, circulation of water to all parts of body takes place due to osmosis.

(ii) Plant roots absorb water from soil due to osmosis. Concentration of cell sap inside the root hair cells is higher than that of water present in the soil. Water enters the root cells due to endosmosis.

(iii) Water absorbed by plant roots is circulated in the entire plant body and reaches to the top of a tall tree due to osmosis.

(iv) Osmosis helps in plant growth and germination of seeds.

(v) Red blood cells burst when placed in water; it is due to endosmosis.

(vi) Various functions of plants are controlled by osmosis, *e.g.*, stretching of leaves and flowers, opening and closing of flowers.

(vii) Use of salt and sugar in pickles and jams acts as preservatives. It prevents growth of bacteria and fungi by osmosis.

(viii) Dead bodies swell under water due to endosmosis.

(ix) When dried fruits and vegetables are placed in water, they slowly swell and return to the original form. It is again due to endosmosis of water into the fruits and vegetables.

Intravenous drip of saline water : Saline drip to the patients is also based on the principle of osmosis.

(i) A 0.91% solution of NaCl in water is isotonic to human blood. Hence, in this solution red blood cells neither swell nor shrink.

(ii) Aqueous solution of NaCl with concentration less than 0.91% is hypotonic to blood. On placing red blood cells in this solution, endosmosis results into bursting of RBCs.

(iii) Aqueous solution of NaCl with concentration more than 0.91% is **hypertonic** to blood. On placing red blood cells in it exosmosis or plasmolysis results into shrinking of cells.

5.14 VAN'T HOFF THEORY OF DILUTE SOLUTIONS

van't Hoff realised that an analogy exists between gases and solutions provided osmotic pressure of solutions is used in place of ordinary gas pressure. He showed that for dilute solutions of non-electrolytes the following laws hold good:

1. Boyle-van't Hoff law: The osmotic pressure (P or π) of a solution is directly proportional to its concentration (C) when the temperature is kept constant. The concentration of the solution containing one gram mole in V litre is equal to $\frac{1}{V}\left(C=\frac{1}{V}\right)$.

Thus, $P \propto C$ (when temperature is constant)

or $P \propto \frac{1}{V}$

or $PV = \text{constant}$ or $\pi V = \text{constant}$

van't Hoff presumed that the osmotic pressure is due to the bombardment of solute molecules against the semipermeable membrane as the gas pressure is due to hits recorded by gas molecules against the walls of its container.

2. Pressure-Temperature law (Gay-Lussac-van't Hoff law): Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T), *i.e.*,

$$P \propto T$$

or $\frac{P}{T} = \text{constant}$ or $\frac{\pi}{T} = \text{constant}$

Combining the two laws, *i.e.*, when concentration and temperature both are changing, the osmotic pressure will be given by:

$$P \propto CT$$

or $P = kCT$

or $P = k \cdot \frac{1}{V} \cdot T$ $\left(\text{since, } C = \frac{1}{V}\right)$

or $PV = ST$ or $\pi V = ST$

S is called molar solution constant.

Here, V is the volume of solution containing one gram mole of the solute. The value of S comes out to 0.082 litre atm K^{-1} mol^{-1} which is in agreement with the value of R, the molar gas constant. In case, the solution contains n gram moles in V litre, the general equation would become:

$$PV = nST \text{ or } \pi V = nST$$

3. Third law: Equimolecular solutions of different solutes exert equal osmotic pressure under identical conditions of temperature. Such solutions which have the same osmotic pressure are termed **isotonic or iso-osmotic.** When two isotonic solutions are separated by a semipermeable membrane, no flow of solvent molecules is observed on either side.

The law is similar to Avogadro's hypothesis. It can be stated as, **"Equal volumes of dilute solutions of different solutes, having the same temperature and osmotic pressure, contain equal number of molecules".**

For solution I, $PV = n_1 ST$

For solution II, $PV = n_2 ST$

Thus, n_1 must be equal to n_2 when P, V and T are same.

The analogy of dilute solutions with gases is thus perfect. This led van't Hoff to suggest **that a solute in dissolved state (*i.e.*, in solution) behaves as a gas and the osmotic pressure of the solution is equal to the pressure which the solute would exert if it were a gas at the same temperature and occupying the same volume as that of the solution.** This statement is known as van't Hoff theory of dilute solutions.

5.15 DETERMINATION OF MOLECULAR MASSES

In the case of dilute solutions, it has been stated that the equation $PV = nST$ holds good. Instead of one gram mole of the solute present in V litre of solution, let w_B gram of solute (mol. mass m_B) be present in V' litre of solution; then

$$n = \frac{w_B}{m_B} \text{ and } V = V'$$

Thus, the equation $PV = nST$ becomes:

$$PV' = \frac{w_B}{m_B} \cdot ST$$

or

$$m_B = \frac{w_B \times S \times T}{PV'}$$

Knowing the value of P experimentally, the value of m_A, *i.e.*, molecular mass of the solute can be determined.

Consider two solutions I and II having n_1 and n_2 moles of the solute in V_1 and V_2 litres of solution respectively. Let P_1 and P_2 be their osmotic pressures at the same temperature (T).

From the equation $PV = nST$,

For solution I, $P_1V_1 = n_1 ST$

or

$$P_1 = \frac{n_1}{V_1} ST$$

For solution II, $P_2V_2 = n_2 ST$

or

$$P_2 = \frac{n_2}{V_2} ST$$

If both solutions are isotonic, *i.e.*, $P_1 = P_2$, obviously,

$$\frac{n_1}{V_1} ST = \frac{n_2}{V_2} ST$$

or

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$

or

$$\frac{w_1/m_1}{V_1} = \frac{w_2/m_2}{V_2}$$

or

$$\frac{w_1}{m_1 \times V_1} = \frac{w_2}{m_2 \times V_2}$$

This is the condition for isotonic solutions.

If molecular mass of one solute is known, the molecular mass of the other can be determined without using osmotic pressure values.

Osmotic pressure of mixture of two solutions:

Case I: Let two solutions of same substance having different osmotic pressures π_1 and π_2 are mixed. Osmotic pressure of the resultant solution can be calculated as,

$$\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$$

where, V_1 and V_2 are the volumes of two solutions and π_R is the resultant osmotic pressure.

Case II: Let n_1 and n_2 are the number of moles of two different solutes present in V_1 and V_2 volumes respectively.

Osmotic pressure of the mixture can be calculated as,

$$\pi = \pi_1 + \pi_2 = \frac{n_1 i_1 RT}{(V_1 + V_2)} + \frac{n_2 i_2 RT}{(V_1 + V_2)}$$

$$\pi = \frac{(n_1 i_1 + n_2 i_2)}{(V_1 + V_2)} RT$$

Here, i_1 and i_2 are van't Hoff factor for the two solutes.

SOME SOLVED EXAMPLES

Example 49. *200 cm^3 of an aqueous solution contains 1.26 g of a polymer. The osmotic pressure of such solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the polymer.*

Solution:

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

$$m_B = \frac{w_B}{V} \times \frac{RT}{\pi}$$

$$= \frac{1.26}{0.2} \times \frac{0.083 \times 300}{2.57 \times 10^{-3}} = 61038 \text{ g mol}^{-1}$$

Example 50. *A solution is prepared by dissolving 1.08 g of human serum albumin, a protein obtained from blood plasma, in 50 cm^3 of aqueous solution. The solution has an osmotic pressure of 5.85 mm Hg at 298 K:*

(*a*) *What is molar mass of albumin?*

(*b*) *What is height of water column placed in solution?*

$$d\,(H_2O) = 1 \text{ g cm}^{-3}$$

Solution: (a) Molar mass of albumin can be calculated using following relation:

$$m_B = \frac{w_B \times RT}{\pi V} \quad \text{...(i)}$$

Given, $w_B = 1.08$ g; $R = 0.0821$ litre atm K^{-1} mol^{-1}

$$T = 298 \text{ K}, \pi = \frac{5.85}{760} \text{ atm}; V = \frac{50}{1000} = 0.05 \text{ litre}$$

Substituting these values in eq. (i)

$$m_B = \frac{1.08 \times 0.0821 \times 298}{(5.85/760) \times 0.05} = 68655 \text{ g/mol}$$

(b)

$$\pi = h \cdot d \cdot g$$

$$\frac{5.85}{760} \times 101325 = h \times 1 \times 10^{-3} \times 9.8$$

$$\therefore \quad h = 7.958 \times 10^4 \text{ m} = 7.958 \times 10^6 \text{ cm}$$

Example 51. *Calculate osmotic pressure of 5% solution of cane sugar (sucrose) at 15°C.*

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

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

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

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

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

$$= 3.453 \text{ atm}$$

Example 52. *The solution containing 10 g of an organic compound per litre showed an osmotic pressure of 1.18 atmosphere at 0°C. Calculate the molecular mass of the compound ($S = 0.0821$ litre atm per degree per mol).*

Solution: Applying the equation,

$$m = \frac{w}{PV} \cdot ST$$

Given, $w = 10$ g, $P = 1.18$ atm, $V = 1$ litre, $S = 0.0821$ and $T = 273$ K.

$$m = \frac{10}{1.18 \times 1} \times 0.0821 \times 273 = 189.94$$

Example 53. *The osmotic pressure of a solution containing 30 g of a substance in 1 litre solution at 20°C is 3.2 atmosphere. Calculate the value of S. The molecular mass of solute is 228.*

Solution: Applying the equation,

$$PV = \frac{w}{m} \cdot ST$$

or

$$S = \frac{m \times P \times V}{w \times T}$$

Given, $m = 228, P = 3.2$ atm, $V = 1$ litre, $w = 30$ g and

$$T = 20 + 273 = 293 \text{ K}$$

$$S = \frac{228 \times 3.2 \times 1}{30 \times 293}$$

$$= 0.083 \text{ litre atm per degree per mol}$$

Example 54. *What is the volume of solution containing 1 g mole of sugar that will give rise to an osmotic pressure of 1 atmosphere at 0°C?*

Solution: Applying the equation $PV = n \cdot ST$,

$$V = \frac{n}{P} \times S \times T$$

Given, $n = 1, P = 1$ atm, $S = 0.0821$ and $T = 273$ K

$$V = \frac{1}{1} \times 0.0821 \times 273 = 22.4 \text{ litre}$$

Example 55. *Find the osmotic pressure of M/20 solution of urea at 27°C ($S = 0.0821$ lit atm K^{-1} mol^{-1}).*

Solution: Applying the equation $PV = n \cdot ST$,

$$P = \frac{n}{V} \cdot ST$$

or

$$P = \text{Molarity} \times S \times T$$

Given,

molarity $= \frac{1}{20} = 0.05, S = 0.0821$ and $T = 27 + 273 = 300$ K

Substituting values,

$$P = 0.05 \times 0.0821 \times 300 = 1.2315 \text{ atm}$$

Example 56. *The osmotic pressure of a solution of an organic substance containing 18 g in one litre of solution at 293 K is 2.414×10^5 Nm^{-2}. Find the molecular mass of the substance if $S = 8.3$ JK^{-1} per mol.*

Solution: Applying the equation,

$$PV = \frac{w}{m} \cdot ST$$

or

$$m = \frac{w}{PV} \cdot ST$$

Given, $P = 2.414 \times 10^5$ $\text{Nm}^{-2}, V = 1.0 \text{ lit} = 1 \times 10^{-3}$ m^3,

$S = 8.3$ JK^{-1} per mol, $w = 18$ g and $T = 293$ K

$$m = \frac{18}{2.414 \times 10^5 \times 1 \times 10^{-3}} \times 8.3 \times 293 = 181.33$$

Example 57. *A 5% solution of cane sugar is isotonic with 0.877% solution of urea. Calculate the molecular mass of urea if the molecular mass of cane sugar is 342.*

Solution: Let the molecular mass of urea be m_2.

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

and

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

For isotonic solutions,

$$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

$$\frac{5}{342 \times 0.1} = \frac{0.877}{m_2 \times 0.1}$$

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

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

32. Find out the osmotic pressure of 0.25 M aqueous solution of urea at 27°C ($R = 0.082$ litre atm K^{-1} mol^{-1}, $R = 1.987$ cal $K^{-1}mol^{-1}$). **[CET (Gujarat) 2008]**

(a) 6.15 atm (b) 0.615 atm (c) 0.0615 atm (d) 61.5 atm

[**Ans.** (a)]

[Hint : $\pi = CRT$

$= 0.25 \times 0.0821 \times 300$

$= 6.157$ atm]

33. Two solutions of glucose have osmotic pressures 1.5 and 2.5 atm. 1 litre of first solution is mixed with 2 litre of second solution. The osmotic pressure of the resultant solution will be:

(a) 1.62 atm (b) 6.12 atm (c) 1.26 atm (d) 2.16 atm

[Ans. (d)]

[Hint: $\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$

$1.5 \times 1 + 2.5 \times 2 = \pi_R \times 3$

$\pi_R = \frac{6.5}{3} = 2.16$ atm]

34. 18 g glucose and 6 g urea are dissolved in 1 litre aqueous solution at 27°C. The osmotic pressure of the solution will be:

(a) 3.826 atm	(b) 4.926 atm
(c) 2.92 atm	(d) 9.42 atm

[Ans. (b)]

[Hint: $\pi V = (n_1 + n_2)RT$

$$\pi V = \left(\frac{w_1}{m_1} + \frac{w_2}{m_2}\right) RT$$

$$\pi \times 1 = \left(\frac{18}{180} + \frac{6}{60}\right) \times 0.0821 \times 300$$

$\pi = 4.926$ atm]

35. A solution containing 10 g per dm^3 of urea (m.w. = 60) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of this non-volatile solute is:

[CBSE (Medical) 2006]

(a) 250 g mol^{-1}	(b) 300 g mol^{-1}
(c) 350 g mol^{-1}	(d) 200 g mol^{-1}

[Ans. (b)]

[Hint: π_1 (urea) $= \pi_2$ (unknown solute)

C_1 (urea) $= C_2$ (unknown solute)

$$\left[\frac{w_B \times 1000}{m_B \times V}\right]_{\text{urea}} = \left[\frac{w_B \times 1000}{m_B \times V}\right]_{\text{unknown solute}}$$

$$\frac{10 \times 1000}{60 \times 1000} = \frac{5 \times 1000}{m_B \times 100}$$

$m_B = 300$ g mol^{-1}]

36. The osmotic pressure of a solution at 0°C is 4 atm. What will be its osmotic pressure at 546 K under similar conditions?

(a) 4 atm (b) 2 atm (c) 8 atm (d) 1 atm

[Ans. (c)]

[Hint: $\frac{\pi_1}{\pi_2} = \frac{CRT_1}{CRT_2}$

$$\frac{\pi_1}{\pi_2} = \frac{T_1}{T_2}$$

$$\frac{4}{\pi_2} = \frac{273}{546}$$

$\pi_2 = 8$ atm]

37. The temperature at which 10% aqueous solution $\left(\frac{W}{V}\right)$ of glucose will exhibit the osmotic pressure of 16.4 atm, is : ($R = 0.082\,dm^3$ atm $K^{-1}mol^{-1}$) **[PMT (Kerala) 2008]**

(a) 360°C (b) 180 K (c) 90 K (d) 300 K

(e) 360 K

[Ans. (e)]

[Hint : $\pi V = nRT$

$$\pi V = \frac{W}{m} RT$$

$$16.4 \times \left(\frac{100}{1000}\right) = \frac{10}{180} \times 0.082 \times T$$

$\therefore$ $T = 360$ K]

5.16 REVERSE OSMOSIS

When a solution is separated from pure water by a semipermeable membrane, water moves towards the solution on account of osmosis. This process continues till osmotic pressure becomes equal to hydrostatic pressure or osmosis can be stopped by applying external pressure equal to osmotic pressure on solution. If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, *i.e.*, in reverse direction of the ordinary osmosis. This type of osmosis is termed **reverse osmosis.** Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.

5.17 ABNORMAL COLLIGATIVE PROPERTIES

The colligative properties of solutions depend on the number of solute particles present in solution. Various relations derived for colligative properties hold good in dilute solutions only when there is no change in molecular state of solute. In case, the total number of particles of the solute changes in solution, the colligative property shall also change accordingly. The number of particles in solution may change in two ways:

(i) By dissociation: When the substance is an electrolyte, *i.e.*, the substance undergoes ionisation and number of particles increases in solution, the ions act as particles. The number of particles, thus, increases on ionisation and the value of colligative property increases accordingly.

(ii) By association: When the substance undergoes association, *i.e.*, two or more molecules of the solute associate to form a single giant particle, the number of particles decreases and consequently the value of colligative property decreases. Thus,

Normal value of colligative property

$\propto$ No. of particles of solute taken

Abnormal value of colligative property

$\propto$ No. of particles of solute after ionisation or association

Thus, the ratio, $\frac{\text{Abnormal colligative property}}{\text{Normal colligative property}}$, may have the value either more than 1 or less than 1. The ratio is termed **van't Hoff factor** which is represented by '*i*'. Thus,

Table 5.6 Illustrations of van't Hoff Factor '*i*' for Different Solutes

S. No.	Solute type	Example	Ionisation or association	No. of particles in the solution from 1 mole solute	van't Hoff factor '*i*'	Abnormal molecular mass
1.	Non-electrolyte	Urea, sucrose, glucose	—	1	1	m_{normal}
2.	Binary electrolyte AB type	NaCl, KCl CH_3COOH, etc.	$\underset{1-\alpha}{AB} \rightleftharpoons \underset{\alpha}{A^+} + \underset{\alpha}{B^-}$	2	$1+\alpha$	$\dfrac{m_{\text{normal}}}{1+\alpha}$
3.	Ternary electrolyte AB_2 type or A_2B type	$CaCl_2$, $BaCl_2$ H_2SO_4, $K_2[PtCl_6]$	$\underset{1-\alpha}{AB_2} \rightleftharpoons \underset{\alpha}{A^{2+}} + \underset{2\alpha}{2B^-}$	3	$1+2\alpha$	$\dfrac{m_{\text{normal}}}{1+2\alpha}$
			$\underset{1-\alpha}{A_2B} \rightleftharpoons \underset{2\alpha}{2A^+} + \underset{\alpha}{B^{2-}}$	3	$1+2\alpha$	$\dfrac{m_{\text{normal}}}{1+2\alpha}$
4.	Quaternary electrolyte AB_3 or A_3B type	$AlCl_3$, $K_3[Fe(CN)_3]$ $FeCl_3$, K_3PO_4	$\underset{1-\alpha}{AB_3} \rightleftharpoons \underset{\alpha}{A^{3+}} + \underset{3\alpha}{3B^-}$	4	$1+3\alpha$	$\dfrac{m_{\text{normal}}}{1+3\alpha}$
			$\underset{1-\alpha}{A_3B} \rightleftharpoons \underset{3\alpha}{3A^+} + \underset{\alpha}{B^{3-}}$	4	$1+3\alpha$	$\dfrac{m_{\text{normal}}}{1+3\alpha}$
5.	Association of solute	Benzoic acid forming dimer in benzene	$\underset{1-\alpha}{nA} \rightleftharpoons \underset{\frac{\alpha}{n}}{An}$	$\dfrac{1}{n}$	$\left[1-\left(1-\dfrac{1}{n}\right)\alpha\right]$	$\dfrac{m_{\text{normal}}}{\left[1-\left(1-\dfrac{1}{n}\right)\alpha\right]}$
6.	General electrolyte AB_{n-1}	One mole of solute giving n ions in the solution	$\underset{1-\alpha}{AB_{n-1}} \rightleftharpoons \underset{\alpha}{A^{+(n-1)}} + \underset{(n-1)\alpha}{(n-1)B^-}$	n	$[1+(n-1)\alpha]$	$\dfrac{m_{\text{normal}}}{[1+(n-1)\alpha]}$

$$i = \frac{P_{\text{obs.}}}{P_{\text{normal}}} = \frac{(\Delta p)_{\text{obs.}}}{(\Delta p)_{\text{normal}}}$$

$$= \frac{(\Delta T_b)_{\text{obs.}}}{(\Delta T_b)_{\text{normal}}} = \frac{(\Delta T_f)_{\text{obs.}}}{(\Delta T_f)_{\text{normal}}}$$

$$= \frac{\text{Actual no. of particles in solution}}{\text{No. of particles taken}}$$

(i) Suppose one molecule of an electrolyte gives '*n*' ions on dissociation and 'α' is its degree of ionisation. Obviously,

Number of ions produced $= n\alpha$

and Number of unionised molecules $= 1-\alpha$

Total number of particles in solution $= 1-\alpha+n\alpha$

$$= 1+(n-1)\alpha$$

Thus,

$$\text{van't Hoff factor '}i\text{'} = \frac{1+(n-1)\alpha}{1} > 1 \text{ if } n \text{ is 2 or more}$$

and
$$\alpha = \frac{i-1}{n-1}$$

(ii) Suppose '*n*' molecules associate to form one giant molecule and 'α' is the degree of association; then

$$\underset{(1-\alpha)}{nA} \rightleftharpoons \underset{\alpha/n}{(A)_n}$$

Total number of particles in solution $= 1-\alpha+\alpha/n$

$$= 1+\left(\frac{1}{n}-1\right)\alpha$$

Thus, $\text{van't Hoff factor '}i\text{'} = \dfrac{1+\left(\dfrac{1}{n}-1\right)\alpha}{1} < 1$ if n is 2 or more

$$\alpha = \frac{1-i}{1-1/n}$$

As, Colligative property $\propto \dfrac{1}{\text{mol. mass}}$

So, $$\frac{\text{Observed colligative property}}{\text{Normal colligative property}} = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

Thus, $$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

In case of dissociation,

$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = 1+(n-1)\alpha > 1$$

Observed mol. mass will always be less than normal mol. mass.

In case of association,

$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = 1+\left(\frac{1}{n}-1\right)\alpha < 1$$

Observed mol. mass will always be higher than normal mol. mass.

Relation between osmotic pressure and vapour pressure

Let an aqueous dilute solution filled in a capillary tube is closed at one end by a semipermeable membrane. The tube is placed in pure solvent (water). Entire apparatus is closed by a belljar. At osmotic equilibrium, the belljar is saturated with water vapour. At equilibrium osmotic pressure (π) becomes equal to hydrostatic pressure.

$$\pi = h \times d \qquad \text{... (i)}$$

where '*h*' is height in the column, π is osmotic pressure.

Let, p_0 = Vapour pressure of pure solvent
p = Vapour pressure of solution

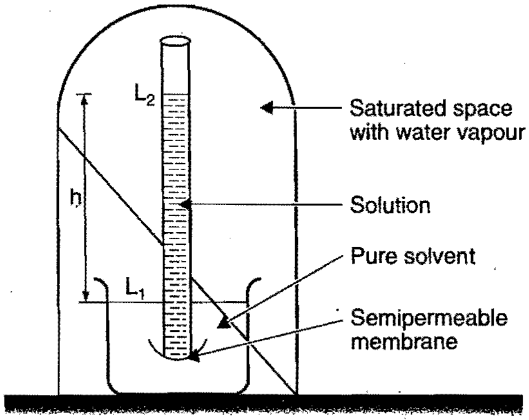


Fig. 5.16

Pressure at level $L_1 = p_0$; Pressure at level $L_2 = p$. Pressure at L_1 will be greater than pressure at L_2. Then

$$p_0 - p = hD \qquad \text{... (ii)}$$

where '*D*' is density of solvent vapour at pressure p_0.

Dividing eq. (i) by eq. (ii), we have,

$$\frac{\pi}{p_0 - p} = \frac{hd}{hD} = \frac{d}{D}$$

at a fixed temperature *d*/*D* is constant.

$$\therefore \qquad \pi = \text{constant}\ (p_0 - p) \qquad \text{... (iii)}$$

$$i.e., \qquad \pi \propto (p_0 - p) \text{ or } \Delta p \qquad \text{... (iv)}$$

Thus, *osmotic pressure is directly proportional to the lowering of vapour pressure.*

We know that,

$$p_0 V = nRT$$

$$p_0 V = \frac{W}{M} RT$$

$$i.e., \qquad p_0 M = \frac{W}{V} RT = DRT$$

$$\therefore \qquad p_0 = \frac{RTD}{M} \qquad \text{... (v)}$$

Dividing eq. (iii) by eq. (v), we get

$$\frac{p_0 - p}{p_0} = \pi \times \frac{D}{d} \times \frac{M}{RTD}$$

$$\frac{\Delta p}{p_0} = \pi \frac{M}{dRT}$$

At a fixed temperature, π and $\frac{M}{dRT}$ is constant.

Thus, $\frac{\Delta p}{p_0} \propto \pi$, *i.e., osmotic pressure is proportional to relative lowering of vapour pressure.*

Partial pressure of immiscible liquids

Let '*A*' and '*B*' be the two volatile and immiscible liquids; p_A and p_B be the partial pressures of '*A*' and '*B*' respectively.

$$\text{Then,} \qquad \frac{p_A}{p_B} = \frac{n_A}{n_B}$$

where, M_A and M_B are molar concentrations of '*A*' and '*B*' respectively.

$$\frac{p_A}{p_B} = \frac{W_A / m_A}{W_B / m_B}$$

where, W_A and W_B are weights of '*A*' and '*B*', m_A and m_B are molecular weights of '*A*' and '*B*' respectively.

Example 58. *Phenol associates in benzene to a certain extent for a dimer. A solution containing* 20×10^{-3} *kg of phenol in* 1.0 *kg of benzene has its freezing point decreased by* 0.69 *K. Calculate the fraction of the phenol that has dimerised* (K_f *of benzene is* 5.12°*K kg mol*$^{-1}$).

Solution: Observed mol. mass

$$= \frac{1000 \times K_f \times w}{W \times \Delta T}$$

$$= \frac{1000 \times 5.12 \times 20 \times 10^{-3}}{1 \times 0.69} = 148.4$$

Normal mol. mass of phenol (C_6H_5OH) = 94

$$\text{So,} \qquad \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = \frac{94}{148.4}$$

$$= 1 + \left(\frac{1}{n} - 1\right)\alpha = 1 + \left(\frac{1}{2} - 1\right)\alpha$$

$$\frac{94}{148.4} = 1 - \frac{\alpha}{2}$$

$$\text{or} \qquad \alpha = 0.733 \quad \text{or} \quad 73.3\%$$

Example 59. *The freezing point depression of* 0.001 *m* $K_x[Fe(CN)_6]$ *is* 7.10×10^{-3} *K. Determine the value of x. Given,* $K_f = 1.86$ *K kg mol*$^{-1}$ *for water.*

Solution:

$$\Delta x = i \times K_f \times m$$

$$7.10 \times 10^{-3} = i \times 1.86 \times 0.001$$

$$i = 3.817$$

$$\alpha = \frac{i - 1}{n - 1}$$

$$1 = \frac{3.817 - 1}{(x + 1) - 1}$$

$$x = 2.817 \approx 3$$

∴ Molecular formula of the compound is $K_3[Fe(CN)_6]$.

Example 60. *A* $\frac{M}{10}$ *solution of potassium ferrocyanide is* 46% *dissociated at* 18°*C. What will be its osmotic pressure?*

Solution: Normal osmotic pressure $= \dfrac{w}{m \times V} \times S \times T$

(when no dissociation has taken place)

$\dfrac{w}{m} = 0.1, V = 1\,\text{litre},\; S = 0.0821, T = 18 + 273 = 291\,\text{K}$

Normal osmotic pressure $= \dfrac{0.1}{1} \times 0.0821 \times 291 = 2.389$ atm

Potassium ferrocyanide is an electrolyte. It dissociates as:

$$\underset{(1-\alpha)}{K_4Fe(CN)_6} \rightleftharpoons \underset{4\alpha}{4K^+} + \underset{\alpha}{[Fe(CN)_6]^{4-}}$$

Total number of particles $= 1 - \alpha + 4\alpha + \alpha = 1 + 4\alpha$

$\alpha = 0.46$; so, $1 + 4\alpha = 1 + 4 \times 0.46 = 2.84$

$$\frac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}} = \frac{2.84}{1}$$

Observed osmotic pressure $= 2.84 \times 2.389$

$= 6.785$ atm

Example 61. *A 0.5% aqueous solution of KCl was found to freeze at $-0.24°$ C. Calculate the van't Hoff factor and degree of dissociation of the solute at this concentration (K_f for water $= 1.86\,K\,kg\,mol^{-1}$).*

Solution: Observed mol. mass of KCl $= \dfrac{1000 \times K_f \times w}{\Delta T \times W}$

Given, $K_f = 1.86\,\text{K kg mol}^{-1}$, $w = 0.5\,\text{g}$, $W = 100\,\text{g}$, $\Delta T = 0.24$

So, Observed mol. mass of KCl $= \dfrac{1000 \times 1.86 \times 0.5}{0.24 \times 100} = 38.75$

Normal mol. mass of KCl $= 39 + 35.5 = 74.5$

$$\text{van't Hoff factor} = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

$$= \frac{74.5}{38.75} = 1.92$$

$$\underset{(1-\alpha)}{KCl} \rightleftharpoons \underset{\alpha}{K^+} + \underset{\alpha}{Cl^-} \quad (\alpha \text{ is the degree of ionisation})$$

Total number of particles $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$i = 1 + \alpha$$

$$1.92 = 1 + \alpha$$

So, $\alpha = 1.92 - 1 = 0.92$

i.e., 92% dissociated.

Example 62. *The freezing point of a solution containing 0.2 g of acetic acid in 20 g of benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene (K_f for benzene is $5.12\,K\,kg\,mol^{-1}$).* **(IIT 1994)**

Solution: Let the observed molecular mass of acetic acid be m_{obs}.

$$m_{\text{obs.}} = \frac{1000 \times K_f \times w}{W \times \Delta T}$$

$$= \frac{1000 \times 5.12 \times 0.2}{20 \times 0.45} = 113.78$$

Normal molecular mass of acetic acid = 60

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

	$2CH_3COOH$	$(CH_3COOH)_2$
Before association	1	0
After association	$(1-\alpha)$	$\alpha/2$

$$\text{van't Hoff factor} = \frac{\text{Normal mol. mass}}{\text{Obs. mol. mass}}$$

$$= \frac{1 - \alpha + \alpha/2}{1}$$

$$\frac{60}{113.78} = 1 - \frac{\alpha}{2}$$

or $\alpha = 0.945$

or 94.5% associated.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

38. 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

[Ans. (c)]

[Hint: $\alpha = \dfrac{i-1}{n-1}$

$$0.9 = \frac{i-1}{2-1};\; i = 1.9$$

$$\pi = iCRT$$

$$= 1.9 \times 0.002 \times 0.082 \times 300$$

$$= 0.094 \text{ bar}]$$

39. A 0.2 molal solution of KCl 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%

[Ans. (b)]

[Hint: $\Delta T = i \times K_f \times m$

$$0.68 = i \times 1.86 \times 0.2$$

$$i = 1.83$$

$$\alpha = \frac{i-1}{n-1}$$

$$= \frac{1.83 - 1}{2 - 1} = 0.83$$

Ionization = 83%]

40. A certain substance 'A' tetramerises in water to the extent of 80%. A solution of 2.5 g of A in 100 g of water lowers the freezing point by 0.3°C. The molar mass of A is:

(a) 122 (b) 31 (c) 244 (d) 62

[Ans. (d)]

[Hint: $\alpha = \dfrac{1-i}{1-\dfrac{1}{n}}$

$$0.8 = \frac{1-i}{1-\dfrac{1}{4}};\; i = 0.4$$

$$\Delta T = iK_f \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{m_B \times 100}$$

$m_B = 62$]

41. van't Hoff factor of Hg_2Cl_2 in its aqueous solution will be (Hg_2Cl_2 is 80% ionized in the solution):

(a) 1.6 (b) 2.6 (c) 3.6 (d) 4.6

[**Ans.** (b)]

[**Hint:** $Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$

$$n = 3$$

$$\alpha = \frac{i-1}{n-1}$$

$$0.8 = \frac{i-1}{3-1}$$

$i = 2.6$]

42. 0.1 *M* aqueous solution of $MgCl_2$ at 300 K is 4.92 atm. What will be the percentage ionization of the salt?

(a) 49% (b) 29% (c) 39% (d) 69%

[**Ans.** (a)]

[**Hint:** $\pi = iCRT$

$$4.92 = i \times 0.1 \times 0.0821 \times 300$$

$$i = 1.99$$

$$\alpha = \frac{i-1}{n-1}$$

$$= \frac{1.99-1}{3-1} = \frac{0.99}{2} = 0.49$$

Percentage ionization = 49%]

43. Which of the following solutions will exhibit highest boiling point? **(KCET 2006)**

(a) 0.01 *M* Na_2SO_4 (b) 0.01 *M* KNO_3

(c) 0.015 *M* urea (d) 0.015 *M* glucose

[**Ans.** (a)]

[**Hint:** $\Delta T = i \times k_b \times m$

$i \times m$ of Na_2SO_4 is highest, hence its boiling point will also be highest.

Na_2SO_4 $i \times m = 3 \times 0.01 = 0.03$

KNO_3 $i \times m = 2 \times 0.01 = 0.02$

Urea $i \times m = 1 \times 0.015 = 0.015$

Glucose $i \times m = 1 \times 0.015 = 0.015$]

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *Calculate the freezing point of an aqueous solution of a non-electrolyte having an osmotic pressure of* 2.0 *atmosphere at* 300 *K.*

$(K_f = 1.86 K\ kg\ mol^{-1}, R = 0.821\ litre\text{-}atm\ K^{-1}\ mol^{-1})$

(IIT 1993)

Solution: We know that,

$$P = CRT$$

or, $$C = \frac{P}{RT} = \frac{2}{0.0821 \times 300} \text{ mol lit}^{-1}$$

In dilute solution, the density of water can be taken as 1.0 g cm^{-3}.

Hence, $$\frac{2}{0.0821 \times 300} \text{ mol lit}^{-1} = \frac{2}{0.0821 \times 300} \text{ mol kg}^{-1}$$

Let ΔT be the depression in freezing point.

$$\Delta T = K_f \times \text{molality}$$
$$= 1.86 \times \frac{2}{0.0821 \times 300} = 0.151 \text{ K}$$

Freezing point = (273 − 0.151) = 272.749 K or − 0.151° C

Example 2. *Calculate the amount of NaCl which must be added to* 100 *g water so that freezing point is depressed by* 2 *K. For water,* $K_f = 1.86 K\ kg\ mol^{-1}$.

Solution: NaCl is a strong electrolyte. It is completely dissociated in solution.

Degree of dissociation, $\alpha = 1$

$$NaCl \rightleftharpoons \underset{(n=2)}{Na^+ + Cl^-}$$

No. of particles after dissociation $= 1 + (n-1)\alpha$

$$= 1 + (2-1) \times 1 = 2$$

$$\frac{\Delta T_{obs.}}{\Delta T_{theo.}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles when there is no dissociation}}$$

$$\frac{2}{\Delta T_{theo.}} = 2$$

or $$\Delta T_{theo.} = 1$$

Let w g of NaCl be dissolved in 100 g of water.

So, $$\Delta T_{theo.} = \frac{1000 \times K_f \times w}{W \times m}$$

or $$w = \frac{\Delta T_{theo.} \times W \times m}{1000 \times K_f} = \frac{1 \times 100 \times 58.5}{1000 \times 1.86}$$

$$= 3.145 \text{ g}$$

Example 3. *The degree of dissociation of* $Ca(NO_3)_2$ *in a dilute solution containing* 14 *g of the salt per* 200 *g of water at* 100°C *is* 70%. *If the vapour pressure of water is* 760 *mm, calculate the vapour pressure of solution.* **(IIT 1991)**

Solution:

$\Delta p_{theo.}$ = Lowering in vapour pressure when there is no dissociation

$$= p_0 \times \frac{wM}{Wm} \quad (\text{given, } p_0 = 760 \text{ mm}, \ w = 14 \text{ g}, \ W = 200 \text{ g}, M = 18, m = 164)$$

$$= \frac{760 \times 14 \times 18}{200 \times 164} = 5.84 \text{ mm}$$

$$\text{Degree of dissociation} = \frac{70}{100} = 0.7$$

$$Ca(NO_3)_2 \rightleftharpoons \underset{(n=3)}{Ca^{2+} + 2NO_3^-}$$

$$\frac{\Delta p_{obs.}}{\Delta p_{theo.}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles when there is no dissociation}}$$

$$= \frac{1 + (n-1)\alpha}{1} = \frac{1 + (3-1) \times 0.7}{1} = 2.4$$

So, $\Delta p_{obs.} = 2.4 \times \Delta p_{theo.} = 2.4 \times 5.84$

$= 14.02$ mm

$$p_0 - p_s = \Delta p_{obs.} = 14.02$$
$$p_s = p_0 - 14.02 = 760 - 14.02 = 745.98 \text{ mm}$$

Example 4. *Calculate the osmotic pressure of solution obtained by mixing* 100 *mL of* 3.4% *solution of urea (molecular mass* = 60) *and* 100 *mL of* 1.6% *solution of cane sugar (molecular mass* = 342) *at* 20°C.

Solution: No. of moles of urea $= \frac{3.4}{60} = 0.0567$

$$\text{No. of moles of cane sugar} = \frac{1.6}{342} = 0.0047$$

Total number of moles = (0.0567 + 0.0047) = 0.0614

Total volume of solution = (100 + 100) = 200 mL

= 0.2 litre

$$PV = (\text{Total number of moles}) \times S \times T$$

$$P = \frac{0.0614}{0.2} \times 0.0821 \times 293 = 7.385 \text{ atm}$$

Example 5. *Calculate the normal boiling point of a sample of sea water found to contain* 3.5% *of NaCl and* 0.13% *of* $MgCl_2$ *by mass. The normal boiling point of water is* 100°C *and* K_b *(water)* $= 0.51 K\ kg\ mol^{-1}$. *Assume that both the salts are completely ionised.*

Solution: Mass of NaCl = 3.5 g

$$\text{No. of moles of NaCl} = \frac{3.5}{58.5}$$

Number of ions furnished by one molecule of NaCl is 2.

So, actual number of moles of particles furnished by sodium chloride $= 2 \times \frac{3.5}{58.5}$

Similarly, actual number of moles of particles furnished by magnesium chloride $= 3 \times \frac{0.13}{95}$

$$\text{Total number of moles of particles} = \left(2 \times \frac{3.5}{58.5} + 3 \times \frac{0.13}{95}\right)$$

$$= 0.1238$$

$$\text{Mass of water} = (100 - 3.5 - 0.13) = 96.37\text{ g} = \frac{96.37}{1000}\text{ kg}$$

$$\text{Molality} = \frac{0.1238}{96.37} \times 1000 = 1.2846$$

$$\Delta T_b = \text{Molality} \times K_b$$

$$= 1.2846 \times 0.51 = 0.655\text{ K}$$

Hence, boiling point of sea water = 373.655 K or 100.655°C.

Example 6. *A solution of a non-volatile solute in water has a boiling point of 375.3 K. Calculate the vapour pressure of water above this solution at 338 K. Given, p_0 (water) = 0.2467 atm at 338 K and K_b for water = 0.52.*

Solution: $\Delta T_b = (375.3 - 373.15) = 2.15\text{ K}$

We know that,

$$\Delta T_b = \text{Molality} \times K_b$$

$$2.15 = \text{Molality} \times 0.52$$

$$\text{Molality} = \frac{2.15}{0.52} = 4.135$$

i.e., 4.135 moles of the solute present in 1000 g of water (55.5 moles).

$$\text{Mole fraction of water} = \frac{55.5}{4.135 + 55.5} = \frac{55.5}{59.635}$$

Vapour pressure of water above solution

$$= \text{Mole fraction} \times p_0$$

$$= \frac{55.5}{59.635} \times 0.2467 = 0.23\text{ atm}$$

Example 7. *Sea water is 3.5% by mass of a salt and has a density 1.04 g cm^{-3} at 293 K. Assuming the salt to be sodium chloride, calculate the osmotic pressure of sea water. Assume complete ionisation of the salt.*

Solution: Mass of NaCl = 3.5 g

$$\text{No. of moles} = \frac{3.5}{58.5}$$

Actual number of moles of particles of solute in solution

$$= \frac{2 \times 3.5}{58.5}$$

$$\text{Volume of solution} = \frac{100}{1.04 \times 1000}\text{ litre}$$

$$\pi = \frac{2 \times 3.5}{58.5} \times \frac{1.04 \times 1000}{100} \times 0.0821 \times 293 = 29.93\text{ atm}$$

Example 8. *Molality of a solution in aqueous medium is 0.8. Calculate its mole fraction and the percentage by mass of solute if molar mass of solute is 60.*

Solution: We know that,

$$m = \frac{x_B \times 1000}{(1 - x_B) \times m_A} \qquad \ldots\text{(i)}$$

where, x_B = mole fraction of solute

m_A = molar mass of solvent

$$0.8 = \frac{x_B \times 1000}{(1 - x_B) \times 18}$$

$$x_B = 0.014$$

Let $w_B = x\text{ g}$, $w_A = 100\text{ g}$

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

$$0.8 = \frac{x \times 1000}{60 \times 100}$$

$$x = 4.8\%$$

Example 9. *Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of $CS_2(l)$ assuming 84% dimerisation of the acid. The boiling point and K_b of CS_2 are 46.2° C and 2.3 K kg mol^{-1} respectively.* **(IIT 1997)**

Solution: $\Delta T = i \times K_b \times \text{Molality}$

$$= i \times K_b \times \frac{w \times 1000}{m \times W}$$

$$\alpha = \frac{1 - i}{1 - 1/n}$$

$$0.84 = \frac{1 - i}{1 - 1/2}$$

$$i = 0.58$$

$$\Delta T = 0.58 \times 2.3 \times \frac{0.61 \times 1000}{122 \times 50} = 0.1334$$

$$T - T_0 = 0.1334$$

$$T = T_0 + 0.1334 = 46.2 + 0.1334 = 46.3334$$

Example 10. *A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.8 mm Hg while that of benzene is 100 mm Hg. Find the molality of the solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene?* **(IIT 1997)**

Solution: $\frac{\Delta p}{p_0} = X_A$

$$\frac{100 - 98.8}{100} = X_A$$

$$X_A = 0.012$$

$$\text{Molality} = \frac{X_A \times 1000}{(1 - X_A)m_B} = \frac{0.012 \times 1000}{0.988 \times 78} = 0.1557$$

$$\Delta T = K_f \times \text{Molality}$$

$$0.73 = K_f \times 0.1557$$

$$K_f = 4.688$$

Example 11. *The solution of a non-volatile solute in water freezes at $-0.30°$ C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and K_f for water is 1.86 degree/molal. Calculate the vapour pressure of this solution at 298 K.* (IIT 1998)

Solution:

$$\Delta T = K_f \times \text{Molality}$$

$$0.3 = 1.86 \times \text{Molality}$$

$$\text{Molality} = 0.161$$

$$\text{Molality} = \frac{X_A \times 1000}{(1 - X_A) \times m_B}$$

$$0.161 = \frac{X_A \times 1000}{(1 - X_A)18}$$

$$X_A = 0.00289$$

$$\frac{\Delta p}{p_0} = X_A$$

$$\frac{23.51 - p_s}{23.51} = 0.00289$$

$$p_s = 23.442 \text{ mm}$$

Example 12. *x g of a non-electrolytic compound (molar mass = 200) is dissolved in 1.0 litre of 0.05 M NaCl solution. The osmotic pressure of this solution is found to be 4.92 atm at 27° C. Calculate the value of 'x'. Assume complete dissociation of NaCl and ideal behaviour of this solution.* (IIT 1998)

Solution:

(i) For NaCl: $\pi = iCRT = 2 \times 0.05 \times 0.0821 \times 300$

$$= 2.463 \text{ atm}$$

(ii) For unknown compound:

$$\pi = CRT = \frac{x}{200} \times 0.0821 \times 300 = 0.1231x \text{ atm}$$

Total osmotic pressure $\pi = \pi_1 + \pi_2$

$$4.92 = 2.463 + 0.1231x$$

$$x = 19.959 \text{ g}$$

Example 13. *The freezing point of a solution containing $50 \, cm^3$ of ethylene glycol in 50 g of water is found to be $-34°$ C. Assuming ideal behaviour, calculate the density of ethylene glycol (K_f for water = $1.86 \, K \, kg \, mol^{-1}$).* (IIT 1999)

Solution:

$$\Delta T = K_f \times \frac{w \times 1000}{m \times W}$$

$$34 = 1.86 \times \frac{w \times 1000}{62 \times 50}$$

$$w = 56.66 \text{ g}$$

$$V = \frac{w}{d}$$

$$50 = \frac{56.66}{d}$$

$$d = 1.13 \text{ g/cm}^3$$

Example 14. *A 1.2% solution of NaCl is isotonic with 7.2% solution of glucose. Calculate the van't Hoff factor of NaCl.* (MLNR 1997)

Solution: NaCl glucose

$$\pi_{(NaCl)} = \pi_{(glucose)}$$

$$iC_1RT = C_2RT$$

$$iC_1 = C_2$$

$$i\left(\frac{1.2/58.5}{V}\right) = \frac{7.2/180}{V}$$

$$i = \frac{7.2 \times 58.5}{1.2 \times 180} = 1.95$$

Example 15. *1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4 K. 2.8 g of solid (A) dissolved in 100 g of benzene gave a solution which froze at 277.76 K. Calculate the molecular mass of (A).* (IIT 2000)

Solution: We know that,

$$\Delta T = K_f \times \frac{w \times 1000}{m \times W}$$

where, ΔT = Depression in freezing point

K_f = Molal depression constant of benzene

w = Mass of solute

m = Molecular mass of solute

W = Mass of solvent

Case I: $(278.4 - 277.12) = K_f \times \dfrac{1.4 \times 1000}{58 \times 100}$

$$1.28 = K_f \times \frac{14}{58} \quad \text{...(1)}$$

Case II: $(278.4 - 277.76) = K_f \times \dfrac{2.8 \times 1000}{m_{(A)} \times 100}$

$$0.64 = K_f \frac{28}{m_{(A)}} \quad \text{...(2)}$$

Dividing eq. (1) by eq. (2), we get

$$m_{(A)} = 232$$

Example 16. *To 500 cm^3 of water, 3.0×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{-3} respectively.* (IIT 2000)

Solution: Mass of solute = 3.0×10^{-3} kg = 3.0 g

Molecular mass of solute = 60

$$\text{Mass of solvent} = 500 \times 0.997 = 498.5 \text{ g}$$

We know that,

$$\text{Degree of dissociation } (\alpha) = \frac{i-1}{n-1}$$

$$0.23 = \frac{i-1}{2-1}$$

or

$$i = 1.23$$

$$\Delta T = i \times K_f \times \text{molality}$$

$$= 1.23 \times 1.86 \times \frac{3 \times 1000}{60 \times 498.5} = 0.229$$

i.e., depression in freezing point = 0.229

Example 17. *Osmotic pressure of a solution is* 1.3 *atm. The density of solution is* $1.1 g/cm^3$. *Calculate osmotic rise.*

$(1\ atm = 76 cm\ Hg, \quad d_{Hg} = 13.6 g/cm^3)$

Solution:

$$\pi = hdg$$

$$1.3 \times 76 \times 13.6 \times g = h \times 1.1 \times g$$

$$h = \frac{1.3 \times 76 \times 13.6}{1.1} \text{ cm}$$

$$= 1221 \text{ cm}$$

Example 18. *(a)* 10 *g of a certain non-volatile solute were dissolved in* 100 *g water at* 20°C. *The vapour pressure was lowered from* 17.3555 *mm to* 17.2350 *mm; calculate the m.wt. of the solute.*

(b) The vapour pressure of pure water at 25°C *is* 23.62 *mm. What will be the vapour pressure of a solution of* 1.5 *g urea in* 50 *g of water?* **(IIT 2001)**

Solution: (a) We know that, $\frac{p_0 - p}{p} = \frac{w_B \times m_A}{m_B \times w_A}$

$$\frac{17.3555 - 17.2350}{17.2350} = \frac{10 \times 18}{m_B \times 100}$$

$$m_B = 258.5$$

(b)

$$p = p_0 x_A$$

$$p = p_0 \frac{n_A}{n_A + n_B} = 23.62 \times \frac{\frac{50}{18}}{\frac{50}{18} + \frac{1.5}{60}}$$

$$p = 23.41 \text{ mm Hg}$$

Example 19. *Match the boiling point with* K_b *for x, y and z if molecular weight of x, y and z are same:*

	b. pt.	K_b
x	100	0.68
y	27	0.53
z	253	0.98

(IIT 2003)

Solution: Molal elevation constant may be calculated as,

$$K_{b_{1000}} = \frac{RT_0^2}{1000 L_V}$$

(where, T_0 = boiling point of pure solvent
L_V = latent heat of vaporization per gram
$L_V = \frac{\Delta H_V}{m_B}$)

$$= \frac{RT_0^2}{1000 \frac{\Delta H_V}{m_B}}$$

(here, ΔH_V = molar latent heat of vaporization
m_B = molar mass of solute)

$$= \frac{RT_0^2 m_B}{1000 \Delta H_V}$$

Since, $\Delta S_V = \frac{\Delta H_V}{T_0}$

$$K_{b_{1000}} = \frac{RT_0\ m_B}{1000 \Delta S_V}$$

here, ΔS_V = entropy of vaporization

By considering ΔS_V as almost constant, $K_b \propto T_0$.

$\therefore \quad K_b(x) = 0.68; \quad K_b(y) = 0.53 \quad$ and $\quad K_b(z) = 0.98$

Example 20. 1.22 *g* C_6H_5COOH *is added into two solvents and data of* ΔT_b *and* K_b *are given as:*

(a) In 100*g* CH_3COCH_3; $\Delta T_b = 0.17$; $K_b = 1.7$ *kg kelvin / mol*

(b) In 100*g benzene;* $\Delta T_b = 0.13$; $K_b = 2.6$ *kg kelvin / mol*

Find out the molecular weight of C_6H_5COOH *in both cases and interpret the result.* **(IIT 2004)**

Solution: (a)

$$\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.17 = 1.7 \times \frac{1.22 \times 1000}{m_B \times 100}$$

$$m_B = 122$$

(normal molecular mass of benzoic acid)

(b)

$$\Delta T = \frac{K_b \times w_B \times 1000}{m_B \times w_A}$$

$$0.13 = \frac{2.6 \times 1.22 \times 1000}{m_B \times 100}$$

$$m_B = 244$$

(Abnormally double molecular mass of benzoic acid, it shows association of benzoic acid in benzene.)

Example 21. *How much* C_2H_5OH *should be added to* 1 *litre* H_2O *so that it will not freeze at* – 20°C?

$K_f = 1.86 °C / m$ **(BCECE 2006)**

Solution: Mass of 1 litre water = 1000 g

$$\because \quad \Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$20 = 1.86 \times \frac{w_B \times 1000}{46 \times 1000}$$

$$w_B = 494.6 \text{ g}$$

Example 22. *Depression in freezing point of* 0.1 *molal solution of HF is* – 0.201°C. *Calculate percentage degree of dissociation of HF.* ($K_f = 1.86 K\ kg\ mol^{-1}$)

[AIPMT (Mains) 2008]

Solution : We know

$$\Delta T = i \times k_f \times m$$

$$0.201 = i \times 1.86 \times 0.1$$

$$i = 1.0806$$

The degree of dissociation HF may be calculated as.

$$\alpha = \frac{i-1}{n-1} = \frac{1.0806-1}{2-1} = 0.0806$$

Percentage dissociation $= \alpha \times 100 = 0.0806 \times 100$

$$= 8.06$$

Example 23. *There is KI and sucrose solution with* 0.1 *M concentration, if the osmotic pressure of KI and sucrose solution is* 0.465 *atm and* 0.245 *atm respectively. Then find the van't Hoff factor of KI and its degree of dissociation.* **[AIPMT (Mains) 2008]**

Solution : For KI

$$\pi = i\,CRT$$

$$0.465 = i \times 0.1 \times RT \qquad \text{...(i)}$$

For Sucrose

$$\pi = CRT$$

$$0.245 = 0.1 \times RT \qquad \text{...(ii)}$$

Dividing eq. (i) by (ii)

$$\frac{0.465}{0.245} = i$$

$$\therefore \quad i = 1.897$$

We know, $\alpha = \dfrac{i-1}{n-1} = \dfrac{1.897-1}{2-1}$

$$= 0.897$$

$\therefore$ Percentage ionization $= 0.897 \times 100$

$$= 89.7$$

Example 24. 102% *solution of glycerine and* 2% *solution of glucose are isotonic. Molecular mass of glucose is* 180 *then find out the molecular mass of glycerine.* **[AIPMT (Mains) 2009]**

Solution : $\pi_{\text{glycerine}} = \pi_{\text{glucose}}$

$$\therefore \quad C_{(\text{glycerine})} = C_{(\text{glucose})}$$

$$\frac{120 \times 1000}{m_{\text{glycerine}} \times 100} = \frac{2 \times 1000}{180 \times 100}$$

$$m_{\text{glycerine}} = 91.8$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Solution: It is a homogeneous mixture of two or more components whose concentration can be varied within certain limits. A solution containing only two components is termed a binary solution. One component is called the solute while other as solvent. The component having the same physical state as the solution is called the solvent. In solutions, in which the two components have the same physical state, the component present in larger proportion is termed the solvent and the other component is called solute.

2. Solubility: A solution is said to be saturated when it contains as much solute as it can dissolve at a particular temperature in presence of the undissolved solute. A super-saturated solution contains more quantity and an unsaturated solution contains less quantity of the solute than a saturated solution.

The amount of the solute in grams which can dissolve at a particular temperature in 100 grams of the solvent when the solution is saturated is termed solubility of the solute.

3. Solubility of a gas in a liquid: Gases which can be easily liquified are more soluble in common solvents. The gases which form ions in water are highly soluble in water. The solubility of a gas generally decreases with rise in temperature and increases with increase in pressure.

Mass of gas dissolved per unit volume of a solvent is directly proportional to the pressure of the gas at a given temperature. This is Henry's law.

$$m = KP \qquad \text{(at constant temperature)}$$

where, m is the mass of gas dissolved per unit volume of solvent, P is pressure of the gas in equilibrium with the solution and K is proportionality constant.

4. Solutions of liquids in liquids: Miscible liquids form three types of solutions which may be ideal or non-ideal solutions.

Ideal solution is that in which the attractive forces among the solute and solvent molecules are of the same order as that of solute intramolecular and solvent intramolecular forces. The ΔH mixing and ΔV mixing in such solutions is zero. Ideal solutions obey Raoult's law.

The solutions in which solute-solvent interactions are different from solute-solute and solvent-solvent interactions are called non-ideal solutions. The non-ideal solutions do not obey Raoult's law for all concentrations.

$\Delta H_{\text{mix}} \neq 0$ and $\Delta V \neq 0$ in these solutions. There are two types of deviations from the ideal behaviour.

(i) If $\Delta V_{\text{mix}} > 0$ and $\Delta H_{\text{mix}} > 0$, then non-ideal solutions show positive deviations. Such solutions form a constant boiling mixture of definite composition (azeotropic mixture) having boiling point less than either of both the liquids. In these solutions solvent-solvent and solute-solute interactions are stronger than solvent-solute interactions. Examples are:

$H_2O + CH_3OH$; $H_2O + C_2H_5OH$; $C_6H_6 + CH_3OH$; $C_6H_6 + CCl_4$; $(CH_3)_2CO + C_6H_6$; $(CH_3)_2CO + C_2H_5OH$.

(ii) If $\Delta V_{\text{mix}} < 0$ and $\Delta H_{\text{mix}} < 0$, then non-ideal solutions show negative deviations. In these solutions, solvent-solvent and solute-solute interactions are weaker than solvent-solute interactions. Such solutions also form azeotropic mixture having boiling point higher than either of the two solvents. Examples are:

$H_2O + HCl$; $H_2O + HNO_3$; $CHCl_3 + (CH_3)_2CO$; $CHCl_3 + C_6H_6$, etc.

5. Methods of expressing the concentration of a solution: Some of the methods are given in the table.

Name	**Symbol**	**Formula**	**Definition**	**Effect of temperature**
1. Mass percentage	% (*W/W*)	$\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$	Number of parts by mass of solute per hundred parts of the solution.	No effect
2. Gram per litre	g/L	$\frac{\text{Mass of solute in grams}}{\text{Volume of solution in litres}}$	Amount of the solute in grams present in one litre of solution.	Changes with change of temperature.
3. Parts per million	ppm	$\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$	Number of parts by mass of solute per 10^6 parts of solution.	No effect
4. Molarity	*M*	$\frac{\text{Number of moles of solute}}{\text{Number of litres of solution}}$	Number of moles of solute per litre of solution.	Changes with change of temperature.
5. Molality	*m*	$\frac{\text{Number of moles of solute}}{\text{Number of kilograms of the solvent}}$	Number of moles of solute present in 1 kg of the solvent.	No effect
6. Normality	*N*	$\frac{\text{Number of gram equivalents of solute}}{\text{Number of litres of solution}}$	Number of gram equivalents of the solute present in one litre of the solution.	Changes with change of temperature.
7. Mole fraction	*X*	$\frac{n_A}{n_A + n_B}$	Ratio of number of moles of one component to the total number of moles of solution.	No effect
8. Formality	*F*	$\frac{\text{Number of formula mass}}{\text{Number of litres of solution}}$	Number of formula mass in grams present per litre of solution.	Changes with change of temperature.

6. Raoult's 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 mole fraction of that constituent in the solution.

$$p_A = \text{mole fraction of } A \times p_A^0 = X_A \times p_A^0$$

In the case of binary solution of two volatile liquids, the total vapour pressure of such solution can be given as:

$$\text{Total vapour pressure of solution} = p_A^0 \times X_A + p_B^0 \times X_B$$
$$= p_A + p_B$$

Mole fraction of component *A* in vapour phase,

i.e., $$Y_A = \frac{p_A}{p} = \frac{p_A^0 X_A}{p_A^0 X_A + p_B^0 X_B}$$

similarly, $$Y_B = \frac{p_B^0 X_B}{p_A^0 X_A + p_B^0 X_B}$$

7. Colligative properties: The properties of dilute solutions containing non-volatile solutes, which depend upon the number of solute particles in solution are called colligative properties. These properties do not depend upon the nature of solutes and solvents. The four colligative properties are:

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

All these properties are dependent on the concentration of solutes in solution.

8. Relative lowering in vapour pressure: When a non-volatile solute is dissolved in a solvent, its vapour pressure decreases. ($p_0 - p_s$) is known as lowering in vapour pressure. $\left(\frac{p_0 - p_s}{p_0}\right)$ is called relative lowering in vapour pressure.

The relative lowering in vapour pressure of a solution containing non-volatile solute is equal to the mole fraction of the solute present in the solution. This is Raoult's law. Mathematically,

$$\frac{p_0 - p_s}{p_0} = X_{\text{solute}} = \frac{n}{n+N}$$

Let w g of the solute (mol. mass = m) be dissolved in W g of solvent (molecular mass = M).

$$\frac{p_0 - p_s}{p_0} = \frac{w/m}{w/m + W/M}$$

If the solution is very dilute w/m in denominator can be neglected.

$$\frac{p_0 - p_s}{p_0} = \frac{w/m}{W/M} = \frac{wM}{mW} \quad \text{or} \quad \frac{\Delta p}{p_0} = \frac{w_A\, m_B}{m_A\, w_B}$$

9. Elevation of boiling point: The boiling point of a solution containing non-volatile solute is always higher than the boiling point of a pure solvent. The increase in boiling point is termed elevation and represented as ΔT_b.

$$\Delta T_b \propto \text{Molality of the solution}$$

or $\Delta T_b = m \times K_b$ (K_b is a molal elevation constant)

or $$\Delta T_b = \frac{1000 \times K_b \times w}{W \times m} \quad \text{or} \quad \Delta T_b = \frac{1000 \times K_b \times w_A}{w_B \times m_A}$$

where, w = mass of solute; m = molecular mass of solute;
W = mass of solvent

K_b is equal to $\dfrac{RT_0^2}{1000L}$.

where, T_0 = boiling point of solvent in absolute scale;

L = latent heat of vaporization

The units of K_b are K kg mol^{-1}.

10. Depression in freezing point: The freezing point of a solution containing non-volatile solute is always less than the freezing point of a pure solvent. The decrease in freezing point is termed depression and represented as ΔT_f.

$$\Delta T_f \propto \text{molality of the solution}$$

or $$\Delta T_f = m \times K_f \qquad (K_f \text{ is a molal depression constant})$$

or $$\Delta T_f = \frac{1000 \times K_f \times w}{W \times m} \text{ or } \Delta T_f = \frac{1000 \times K_f \times w_A}{w_B \times m_A}$$

where, w = mass of solute; m = molecular mass of solute;

W = mass of solvent

K_f is equal to $\dfrac{RT_0^2}{1000L}$.

where, T_0 = freezing point of solvent in absolute scale;

L = latent heat of fusion

The units of K_f are K kg mol^{-1}.

11. Osmosis and osmotic pressure: When a solution is separated from the pure solvent with the help of a semipermeable membrane, the solvent molecules from the pure solvent move towards the solution. The movement of solvent molecules from low concentration to higher concentration through semipermeable membrane is termed as osmosis.

As a result of osmosis, a pressure is developed which is termed as osmotic pressure, *i.e.*, the hydrostatic pressure which develops on account of osmosis is called osmotic pressure. It is equal to $h \cdot d \cdot g$. It is also found that if an equal and opposite force is applied on the solution, the osmosis stops. Thus, the excess pressure that must be applied on the solution as to prevent osmosis is also the measure of osmotic pressure.

Osmotic pressure of a dilute solution is given by van't Hoff equation, $P = CRT$, where C = concentration, R = solution constant and T = absolute temperature.

$$C = \frac{n}{V} = \frac{w}{m \times V}$$

where, w = mass of solute in grams

V = volume of solution in litres

m = molecular mass of solute

i.e., $$P = \frac{w}{m \times V} \cdot RT$$

Best method for the determination of osmotic pressure is Berkeley and Hartley's method.

The term hypertonic and hypotonic are applied to compare the osmotic pressures of two solutions. The solution having lower osmotic pressure is termed hypotonic and the solution having higher osmotic pressure is termed hypertonic solution. The two solutions having equal osmotic pressures are termed as isotonic. Condition for isotonic solutions is

$$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

A 0.91% solution of pure NaCl is isotonic with human blood cells (RBC). An NaCl solution with concentration less than 0.91% is called hypotonic and RBC will swell and burst in the solution. An NaCl solution with concentration greater than 0.91% is called hypertonic and RBC will shrink in this solution, *i.e.*, will undergo **plasmolysis or crenation.**

12. van't Hoff factor: When the solute undergoes dissociation or association in solution, the number of particles in solution increases or decreases and thus, the colligative property changes accordingly. In 1886, van't Hoff introduced a factor 'i' known as van't Hoff factor to express the extent of dissociation or association of the solute in solution.

van't Hoff factor, i

$$= \frac{\text{Observed colligative property}}{\text{Theoretical or normal colligative property}}$$

$$= \frac{\text{No. of particles after dissociation or association}}{\text{No. of particles when there is no dissociation or association}}$$

$$= \frac{\text{Normal molecular mass of the solute}}{\text{Observed molecular mass of the solute}}$$

From the value of 'i' it is possible to determine the degree of dissociation or association.

In case of dissociation 'i' is greater than 1.

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

where, n is the number of particles per molecule and α is the degree of dissociation.

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

Similarly, in case of association, 'i' is less than 1.

$$i = \frac{1 + \left(\frac{1}{n} - 1\right)\alpha}{1}$$

where, n is the number of molecules which are associated to form one giant molecule and α is the degree of association.

or $$\alpha = \frac{i-1}{\left(\frac{1}{n} - 1\right)}$$

Molecular masses of electrolytes observed by the methods based on colligative properties are always less than normal molecular masses.

13. Calculation of osmotic pressure from lowering of vapour pressure:

$$\frac{P_0 - P}{P_0} = \frac{\pi m_B}{RdT}$$

where, P_0 = vapour pressure of pure solvent

P = vapour pressure of solution

π = osmotic pressure

m_B = molecular mass of solvent

d = density of solution in $\mathrm{gmL^{-1}}$

R = gas constant in atm mL / deg / mol, *i.e.*, 82.1 .

14. Variation of vapour pressure with temperature (Clausius-Clapeyron equation):

$$\log_{10}\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where, P_1 = vapour pressure at T_1

P_2 = vapour pressure at T_2

ΔH = latent heat of vaporization per mole

15. Variation of vapour pressure of a liquid with external pressure:

$$\log_{10}\left(\frac{p_2}{p_1}\right) = \frac{V_l}{2.303RT}(P_2 - P_1)$$

where, p_1 = vapour pressure at external pressure P_1

p_2 = vapour pressure at external pressure P_2

V_l = molar volume of liquid.

16. Molecular masses of polymers are best determined by osmotic pressure method because other colligative properties give so low value that they cannot be measured accurately.

17. To avoid the freezing of water in a car radiator, in the sub-zero weather, ethylene glycol is added to lower the freezing point of water.

18. Freezing point is same as melting point. Hence, instead of depression in freezing point, depression in melting point can be determined. For this purpose camphor is used as solvent because it has high molal depression constant, *i.e.*, $40\,\mathrm{K\,m^{-1}}$.

19. Relationship between different colligative properties:

(i) Osmotic pressure π and boiling point elevation ΔT_b:

$$\pi = \Delta T_b \times \frac{dRT}{1000K_b}$$

(ii) Osmotic pressure π and freezing point depression ΔT_f :

$$\pi = \Delta T_f \times \frac{dRT}{1000K_f}$$

(iii) Elevation in boiling point and relative lowering of vapour pressure:

$$\Delta T_b = \frac{1000K_b}{m_A} \times \frac{\Delta P}{P_0}; \quad m_A = \text{molar mass of solvent}$$

(iv) Depression in freezing point and relative lowering of vapour pressure:

$$\Delta T_f = \frac{1000K_f}{m_A} \times \frac{\Delta P}{P_0}.$$

20. Hygroscopic and deliquescent substances both absorb moisture from the air. The former do not change their state, *e.g.*, glycerol, whereas the latter dissolve into it, *e.g.*, NaOH. They absorb moisture because the vapour pressure of their saturated solution is less than that of water vapours present in surroundings at that temperature.

The substances like $\mathrm{Na_2CO_3 \cdot 10H_2O}$ which lose their water of crystallisation are called **efflorescent.**

Questions

1. Match the following:

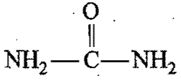
Set-I	**Set-II**
(A) 10 vol H_2O_2	1. Perhydrol
(B) 20 vol H_2O_2	2. 5.358 N
(C) 30 vol H_2O_2	3. 1.785 N
(D) 100 vol H_2O_2	4. 3.03 %

The correct match is :

(a) A – 4, B – 3, C – 2, D – 1
(b) A – 1, B – 2, C – 3, D – 4
(c) A – 1, B – 3, C – 2, D – 4
(d) A – 4, B – 2, C – 3, D – 1 **[CPMT (UP) 2008]**

2. Matrix Matching Problems (For IIT aspirants):

[A] Match the solutes in Column-I with the van't Hoff factors in Column-II:

Column-I	**Column-II**
(a) $K_4[Fe(CN)_6]$	(p) $1+\alpha$
(b) $Al_2(SO_4)_3$	(q) Greater than 1
(c)  $NH_2—\overset{\overset{\large O}{\parallel}}{C}—NH_2$	(r) $(1+4\alpha)$
(d) $CaCl_2$	(s) 1

α = Degree of ionization.

[B] Match the solutions in Column-I with their nature in Column-II:

Column-I	**Column-II**
(a) Benzene + toluene	(p) Non-ideal solution
(b) Ethanol + water	(q) Ideal solution
(c) Benzene + chloroform	(r) $\Delta H_{mix} > 0$
(d) Carbon tetrachloride + chloroform	(s) $\Delta H_{mixing} = 0$

[C] Match the solutions in Column-I with their nature in Column-II:

Column-I	**Column-II**
(a) n-hexane + n heptane	(p) Can be perfectly separated by distillation
(b) Acetone + chloroform	(q) Maximum boiling azeotrope
(c) Acetone + aniline	(r) Cannot be perfectly separated by distillation
(d) Ethanol + water	(s) Nearly ideal

[D] Match the solutions in Column-I with their osmotic properties in Column-II:

Column-I	**Column-II**
(a) S_1: 0.1 M glucose, S_2: 0.1 M urea	(p) S_1 and S_2 are isotonic
(b) S_1: 0.1 M NaCl, S_2: 0.1 M Na_2SO_4	(q) No migration of solvent across the membrane
(c) S_1: 0.1 M NaCl, S_2: 0.1 M KCl	(r) S_1 is hypertonic to S_2
(d) S_1: 0.1 M $CuSO_4$, S_2: 0.1 M sucrose	(s) S_1 is hypotonic to S_2

[**Note:** Assume that the electrolytes are completely ionised.]

[E] Match the solutions in Column-I with their colligative properties in Column-II:

Column-I	**Column-II**
(a) 0.1 M $Ca_3(PO_4)_2$	(p) Solution with highest boiling point
(b) 0.1 M NaCl	(q) Solution with van't Hoff factor greater than 1
(c) 0.1 M glucose	(r) Solution with lowest osmotic pressure
(d) 0.1 M $CaCl_2$	(s) Solution with lowest freezing point

[**Note:** Assume that the electrolytes are completely ionised.]

[F] Match the concentration terms of List-I with their informations in List-II:

List-I	**List-II**
(a) Molarity	(p) Number of gram formula mass of solute dissolved per litre of solution
(b) Molality	(q) Number of moles of solute dissolved per kg of solvent
(c) Formality	(r) Depends on temperature
(d) Strength of solution	(s) Number of moles of solute dissolved per litre of solution

Answers

1. (a) A-4, B-3, C-2, D-1.

2. [A] (a—q, r); (b—q, r); (c—s); (d—p, q)
[B] (a—q, s); (b—p, r); (c—p); (d—s)
[C] (a—p, s); (b—q, r); (c—q, r); (d—r)
[D] (a—p, q); (b—s); (c—p, q); (d—r)
[E] (a—p, q, s); (b—q); (c—r); (d—q)
[F] (a—r, s); (b—q); (c—p, r); (d—r)

• PRACTICE PROBLEMS •

1. 15 g of methyl alcohol is present in 100 mL of solution. If the density of solution is 0.96 g mL^{-1}, calculate the mass percentage of methyl alcohol in solution.

[**Ans.** 15.625%]

2. A solution is prepared by dissolving 15 g of cane sugar in 60 g water. Compute the mass per cent of each component of solution.

[**Ans.** Mass percentage of sugar 20%, Mass percentage of water 80%]

3. The density of the solution of a salt X is 1.15 g mL^{-1}. 20 mL of the solution when completely evaporated gave a residue of 4.6 g of the salt. Calculate the mass percentage of the solute in solution.

[**Ans.** 20%]

4. (a) 5.85 g of NaCl is dissolved in 200 mL of water. What will be the molarity of this solution?

[**Ans.** 0.5 M]

(b) Calculate the molarity of the solution obtained by dissolving 20.6 g NaBr in 500 mL of water.

[**Ans.** 0.4 M]

5. The density of a solution containing 40% by mass of HCl is 1.2 g/mL. Calculate the molarity of the solution.

[**Ans.** 13.15 M]

6. Concentrated sulphuric acid has density of 1.9 g/mL and 99% H_2SO_4 by mass. Calculate the molarity of the acid.

[**Ans.** 19.19 M]

7. A mixture of alcohol and water contains 54% water by mass. Calculate the mole fraction of alcohol in this solution.

[**Ans.** 0.25]

8. What amount of oxalic acid is required to prepare 250 mL 0.1 N solution (Given: molecular mass of oxalic acid = 126)?

[**Ans.** 1.575 g]

9. 7.45 g of potassium chloride is dissolved in 100 g of water. What will be the molality of the solution?

[**Ans.** 1 m]

10. A solution is prepared by mixing 50 g sugar in 100 g of water at 25° C. Calculate the following:

(i) Mass per cent of water.
(ii) Mole fraction of sugar.
(iii) Molality of the solution.

[**Ans.** (i) 66.6 (ii) 0.0256 (iii) 1.46 m]

11. A solution contains 25% water, 50% ethanoic acid and 25% ethanol by mass. Compute the mole fraction of each component:

[**Ans.** Mole fraction of water = 0.5022;
Mole fraction of ethanoic acid = 0.3013;
Mole fraction of ethanol = 0.1965]

12. Find the amount of 98% pure Na_2CO_3 required to prepare 5 litres of 2 N solution.

[**Ans.** 540.8 g impure Na_2CO_3]

13. Calculate the final molarity when 2.0 litre of 3.0 M sugar solution and 3.0 litre of 2.5 M sugar solution are mixed and then diluted to 10 litres with water.

[**Hint:** After mixing number of moles of sugar present $= 2 \times 3 + 3 \times 2.5 = 13.5$; Final molarity $= \frac{13.5}{10} = 1.35\,M$]

14. If 20.0 mL of 1.0 M calcium chloride and 60 mL of 0.2 M $CaCl_2$ are mixed, what will be the molarity of the final solution?

[**Ans.** 0.40 M]

15. Calculate the molarity of each of the ions in a solution when 3.0 litre of 4.0 M NaCl and 4.0 litre of 2.0 M $CoCl_2$ are mixed and diluted to 10 litre.

[**Ans.** Molarity $Na^+ = 1.2\,M$; Molarity $Co^{2+} = 0.8\,M$; Molarity $Cl^- = 2.8\,M$]

[**Hint:**

$$\begin{array}{ccccc} NaCl & = & Na^+ & + & Cl^- \\ \text{1 mole} & & \text{1 mole} & & \text{1 mole} \\ 3 \times 4 \text{ mole} & & \text{12 mole} & & \text{12 mole} \\ CoCl_2 & = & Co^{2+} & + & 2Cl^- \\ \text{1 mole} & & \text{1 mole} & & \text{2 mole} \\ 2 \times 4 \text{ mole} & & \text{8 mole} & & \text{16 mole} \end{array}$$

Total Cl^- ions = 28 mole]

16. What volume of 96% H_2SO_4 solution (density 1.83 g/mL) is required to prepare 4 litre of 3.0 M H_2SO_4 solution?

[**Ans.** 670 mL]

[**Hint:** First determine the molarity of 96% H_2SO_4 and then dilute to get the desired solution.]

17. Calculate the molarity of each ion in solution after 2.0 litre of 3.0 M $AgNO_3$ is mixed with 3.0 litre of 1.0 M $BaCl_2$.

[**Ans.** Molarity of $Ba^{2+} = 0.6\,M$; Molarity of $NO_3^- = 1.2\,M$]

[**Hint:**	$BaCl_2$ +	$2AgNO_3$ =	$2AgCl \downarrow + Ba(NO_3)_2$
Initial	3 mole Ba^{2+}	6 mole Ag^+	6 mole Ag^+ will react with 6 mole Cl^- to form AgCl(s)
	6 mole Cl^-	6 mole NO_3^-,	
After reaction	3 mole Ba^{2+}	6 mole NO_3^-	

Total volume 3.0 + 2.0 = 5 litre.]

18. The density of a 10.0% by mass of KCl solution in water is 1.06 g/mL. Calculate molarity, molality and mole fraction of KCl in this solution.

[**Ans.** Molarity = 1.42 M; Molality = 1.489 m; mole fraction of KCl = 0.026]

19. Calculate the molality and mole fraction of the solute in an aqueous solution containing 6 g of urea per 500 g of water (Mol. mass of urea = 60).

[**Ans.** Molality = 0.2 M; Mole fraction = 0.00359]

20. Calculate the molality of 1 litre solution of 93% H_2SO_4 (mass/volume). The density of the solution is 1.84 g/mL. **(MLNR 1993)**

[**Ans.** 10.428 m]

21. Molarity of H_2SO_4 is 0.8 and its density is 1.06 g/cm^3. What will be its concentration in terms of molality and mole fraction. **[CBSE (Mains) 2005]**

[**Ans.** $m = 0.814$; $x_{H_2SO_4} = 0.014$]

22. A 6.90 M solution of KOH in water contains 30% by mass of KOH. Calculate the density of the solution.
[**Ans.** 1.288 g mL^{-1}]

23. How many kilograms of wet NaOH containing 10% water are required to prepare 60 litre of a 0.5 M solution?
[**Ans.** 1.33 kg]

24. In an experiment, 18.0 g of mannitol was dissolved in 100 g of water. The vapour pressure of solution at 20° C was 17.226 mm of mercury. Calculate the molecular mass of mannitol. The vapour pressure of water at 20° C is 17.535 mm of mercury.
[**Ans.** Molecular mass of mannitol = 181.02]

25. The vapour pressure of water at 20° C is 17.53 mm. Calculate the vapour pressure of a solution at 20° C containing 6 g of urea in 100 g of water (molecular mass of urea = 60).
[**Ans.** Vapour pressure of solution = 17.22 mm]

26. The vapour pressure of ether (molecular mass = 74) is 442 mm Hg at 293 K. If 3 g of a compound A are dissolved in 50 g of ether at this temperature, the vapour pressure falls to 426 mm Hg. Calculate the molecular mass of A assuming that the solution of A is very dilute.
[**Ans.** $m = 123$]

27. 18.2 g of urea is dissolved in 100 g of water at 50° C. The lowering of vapour pressure produced is 5 mm Hg. Calculate the molecular mass of urea. The vapour pressure of water at 50° C is 92 mm Hg.
[**Ans.** 57.05]
[**Hint:** Use $\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$, as the solution is not very dilute]

28. Calculate the vapour pressure of a solution at 100° C containing 3 g of cane sugar in 33 g of water.
[**Ans.** 756.36 mm of Hg]
[**Hint:** Apply $\frac{p_0 - p_s}{p_0} = \frac{wM}{Wm}$ as the solution is very dilute.
$p_0 = 760$ mm of Hg at 100° C and $m = 342$]

29. An aqueous solution containing 28% by mass of a liquid A (molecular mass = 140) has a vapour pressure of 160 mm at 37° C. Find the vapour pressure of pure liquid A (the vapour pressure of water at 37° C is 150 mm).
[**Ans.** $p_A = 358.3$ mm]
[**Hint:** Apply P_{total} = mole fraction of liquid $A \times p_A$ + mole fraction of water $\times p_w$. Mass of water = 100 − 28 = 72 g]

30. At 25° C, the vapour pressure of pure benzene is 100 torr, while that of pure ethyl alcohol is 44 torr. Assuming ideal behaviour, calculate the vapour pressure at 25° C of a solution which contains 10 g of each substance.
[**Ans.** 64.775 torr]

31. Estimate the lowering of the vapour pressure due to solute in a 1.0 molal aqueous solution at 100° C.
[**Ans.** 14 mm of Hg or 14 torr]

32. Find the molality of a solution containing a non-volatile solute if the vapour pressure is 2% below the vapour pressure of pure water. **(Dhanbad 1990)**
[**Ans.** 1.133 m]

33. Calculate the mass of a non-volatile solute of molecular mass 40, which should be dissolved in 114 g of octane to reduce the vapour pressure to 80%.
[**Ans.** 10 g]

34. 10 g of a certain non-volatile solute was dissolved in 100 g of water at 20° C. The vapour pressure was lowered from 17.3555 to 17.235 mm. Calculate the molecular mass of the solute.
[**Ans.** 257.45]

35. 0.534 g of solute is dissolved in 15 g of water then freezing point temperature changes from 0°C to −1.57°C. Molal depression constant of water, $K_f = 1.85$ K kg mol^{-1}. Find out:
(i) Molal concentration
(ii) Molecular mass of solute **[AIPMT (Mains) 2009]**
[**Ans.** (i) 0.848 (ii) 41.98 amu]

36. Addition of 0.643 g of a compound to 50 mL of benzene (density 0.879 g/mL) lowers the freezing point from 5.51° C to 5.03° C. If K_f for benzene is 5.12, calculate the molecular mass of the compound. **(IIT 1992)**
[**Ans.** 156]

37. A solution made by dissolving 0.32 g of a new compound in 25 g of water has freezing point − 0.201°C. Calculate the molecular mass of the new compound.
[**Ans.** 118.4]

38. The boiling point of a solution of 0.1050 g of a substance in 15.84 g of ether was found to be 0.1° C higher than that of pure ether. What is the molecular mass of the substance (Molecular elevation constant of ether per 100 g is 21.6)? **(MLNR 1991)**
[**Ans.** 143.18]

39. Calculate the freezing point and the boiling point at 1 atmosphere of a solution containing 30 g cane sugar (molecular mass 342) and 150 g water.
Given: $K_b = 0.513$ and $K_f = 1.86$.
[**Ans.** Boiling point = 100.3; Freezing point = − 1.09°C]

40. When 36.0 g of a solute having the empirical formula CH_2O is dissolved in 1.20 kg of water, the solution freezes at − 0.93° C. What is the molecular formula of the compound?
[**Ans.** $C_2H_4O_2$]

41. In winter, the normal temperature in Kullu valley was found to be − 11° C. Is a 28% (by mass) aqueous solution of ethylene glycol suitable for a car radiator?
K_f for water = 1.86 K kg mol^{-1}.
[**Ans.** Yes. The given solution freezes at − 11.66° C]

42. Latent heat of fusion of water is 80 cal/g and its normal freezing point is 0° C. Calculate molal depression constant for water. (R = 1.987 cal)
[**Ans.** 1.86 K kg mol^{-1}]

43. A solution containing 7.5 g of urea (molecular mass = 60) in 1 kg of water freezes at the same temperature as another solution containing 15 g of solute 'A' in the same amount of water. Calculate molar mass of 'A'.
[**Ans.** 120]

44. Calculate the osmotic pressure of a decinormal solution of NaCl which is ionised to 80% at 27° C.
[**Ans.** 4.43 atm]

45. What is the volume of a solution containing 2 g mole of sugar that will give rise to an osmotic pressure of 1 atmosphere at STP?
[**Ans.** 44.8 litre]

46. If the osmotic pressure of 5 g per litre solution of a compound at 27° C is 0.025 atm, calculate the molecular mass of the compound.

[**Ans.** 4926]

47. The osmotic pressure of blood is 7.65 atmosphere at 37° C. How much glucose should be used per litre for an intravenous injection that is to have same osmotic pressure as blood?

[**Ans.** 54.18 g of glucose per litre]

48. 10 g of cane sugar (molecular mass = 342) in 1×10^{-3} m^3 of solution produces an osmotic pressure of 6.68×10^4 Nm^{-2} at 273 K. Calculate the value of S in SI units.

[**Hint:** $$S = \frac{PV}{n \times T}$$

Given: $V = 1 \times 10^{-3}$ m^3; $P = 6.68 \times 10^4$ Nm^{-2};

$$n = \frac{10}{342}, T = 273$$

$$S = \frac{6.68 \times 10^4 \times 1 \times 10^{-3} \times 342}{10 \times 273} = 8.3684 \text{ J K}^{-1} \text{ mol}^{-1}]$$

49. A 250 mL water solution containing 48 g of sucrose (molecular mass = 342) at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied on solution as to prevent osmosis?

[**Ans.** 13.8 atm]

50. What would be the osmotic pressure of 0.05 M solution of sucrose at 5° C? Find out the concentration of a solution of glucose which would be isotonic with this solution of sucrose. (Molecular mass of sucrose = 342, Molecular mass of glucose = 180)

[**Ans.** 1.14 atm; Concentration of glucose soln. = 9.0 g/L]

51. Calculate the osmotic pressure of 0.5% solution of glucose (molecular mass 180) at 18° C. The value of solution constant is 0.0821 litre-atm K^{-1} mol^{-1}.

[**Ans.** 0.6628 atm]

52. 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. Determine extent of dilution.

[**Hint:** Original solution $$\frac{500}{760} \times V_1 = \frac{w}{m} \times S \times 283 \quad \text{...(i)}$$

After dilution $$\frac{105.3}{760} \times V_2 = \frac{w}{m} \times S \times 298 \quad \text{...(ii)}$$

or $$\frac{V_2}{V_1} \times \frac{105.3}{500} = \frac{298}{283}$$

or $$\frac{V_2}{V_1} = \frac{298}{283} \times \frac{500}{105.3} = 5$$

i.e., the solution is diluted to the extent that V_2 is five times the original volume (V_1).]

53. Two solutions containing respectively 0.75 g of urea (molecular mass 60) and 1.5 g compound X in 100 g of water boil at the same temperature. Calculate the molecular mass of X.

[**Ans.** 120]

54. A 5% solution of glucose is isotonic with 1.1% solution of KCl at 30° C. Calculate the degree of ionisation of KCl.

[**Ans.** 0.88 or 88%]

55. What should be the osmotic pressure of a solution of urea in water at 30° C which has boiling point 0.052 K higher than pure water? Assume molarity and molality to be the same. K_b for water is 0.52 K kg mol^{-1}.

[**Ans.** 2.487 atm]

56. 4.0 g of a substance A dissolved in 100 g H_2O depressed the freezing point of water by 0.1° C while 4.0 g of another substance B depressed the freezing point by 0.2° C. Which one has higher molecular mass and what is the relation?

[**Ans.** $M_A = 2M_B$]

57. A solution containing 28 g of phosphorus in 315 g of CS_2 (boiling point 46.3° C) boils at 47.98° C. The molal elevation constant for CS_2 is 2.34 K kg mol^{-1}. Calculate the molecular mass of phosphorus and deduce its formula in CS_2.

[**Ans.** 123.8, P_4]

58. A solution of two volatile liquids A and B obeys Raoult's law. At a certain temperature it is found that when the pressure above the mixture in equilibrium is 402.5 mm of Hg, the mole fraction of A in the vapour is 0.35 and in the liquid it is 0.65. What are the vapour pressures of two liquids at this temperature?

[**Hint:** Let p_A and p_B be the partial pressures of vapours and p_A^0 and p_B^0 be the vapour pressures of two liquids respectively.

$$p_A = 0.65\, p_A^0 \quad \text{and} \quad p_B = 0.35 p_B^0$$

$$p_A + p_B = 402.5 \quad \text{(given)}$$

In vapour phase,

$$\frac{p_A}{p_A + p_B} = 0.35 \quad \text{or} \quad p_A = 0.35 \times 402.5 = 140.875 \text{ mm}$$

So, $p_A^0 = 216.72$ mm and $p_B^0 = 747.5$ mm]

59. Calculate the amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g water to -9.3° C (K_f for water = 1.86 K kg mol^{-1}). (IIT 1995)

[**Hint:** $$\Delta T = K_f \times m$$

$$9.3 = 1.86 \times m$$

or $$m = 5$$

Thus, solution of 5.0 molality will have freezing point of -9.3° C. Let W g water be needed to prepare 5.0 molal solution containing $\frac{50}{62}$ mole of ethylene glycol.

So, $$\frac{50 \times 1000}{62 \times W} = 5.0$$

or $$W = \frac{50 \times 1000}{62 \times 5} = 161.3 \text{ g}$$

Hence, ice separating out = (200 − 161.3) = 38.7 g]

60. At 293.2 K, the density of a 60% aqueous solution of methanol is 0.8946 g/mL. Calculate volume of 1 mole of the solution.

[**Ans.** 28.46 mL/mol]

[**Hint:** Let volume of solution be 100 mL

$$W = 100 \times 0.8946 = 89.46 \text{ g}$$

$$n_{CH_3OH} = \frac{60}{32} = 1.875$$

$$n_{H_2O} = \frac{29.46}{18} = 1.636$$

Total moles = 1.875 + 1.636 = 3.511

Volume per mole $= \dfrac{100}{3.511} = 28.48$ mL/mol]

61. 1.2 kg ethylene glycol $\left(\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}\right)$ was added in a car radiator containing 9 litre water. The freezing of water was just prevented when car was running in the Himalayan valley at temperature -4°C. Sudden thunderstorm in the valley lowered the temperature to -6°C. Calculate the amount of ice separated.

[**Ans.** 3 kg ice]

[**Hint:** $\Delta T = K_f \times \dfrac{w_A \times 1000}{m_A \times w_B}$ $A \rightarrow$ Solute; $B \rightarrow$ Solvent

$$6 = 1.86 \times \frac{1200 \times 1000}{62 \times w_B}$$

$$w_B = 6000 \text{ g}$$

$$I_{\text{Weight of ice}} = \text{Total weight of } H_2O - \text{wt. of } H_2O \text{ at } -6°C$$
$$= 9000 - 6000 = 3000 \text{ g} = 3 \text{ kg}]$$

62. 2 g mixture of glucose and sucrose is dissolved in 1 litre water at 298 K to develop osmotic pressure of 0.207 atm. Calculate percentage composition of glucose and sucrose by mole as well as by mass.

[**Ans.**
Percentage by mole: glucose = 65.194, sucrose = 34.806;
Percentage by mass: glucose = 50, sucrose = 50.]

63. If benzoic acid (mol. mass = 122) is associated into double molecules when dissolved in benzene and the osmotic pressure of a solution of 5 g of benzoic acid in 100 mL benzene is 5.73 atm at 10°C, what is the percentage association of benzoic acid?

[**Ans.** 80%]

[**Hint:** $\pi = iCRT = i\dfrac{n}{V}RT$

$$5.73 = i \times \frac{5/122}{0.1} \times 0.0821 \times 283$$

$$i = 0.6017$$

$$\alpha = \frac{1-i}{1-1/n} = \frac{1-0.6017}{1-1/2} \approx 0.8$$

% association = 80%]

64. 0.1 formal solution of NaCl is found to be isotonic with 1.10% solution of urea. Calculate the apparent degree of ionization of NaCl.

[**Ans.** 0.83]

[**Hint:** $\pi_{\text{NaCl}} = \pi_{\text{urea}}$

$$= n \times \frac{1}{V} RT$$

$$i \times 0.1 \times RT = \frac{1.1}{60 \times 0.1} \times RT \qquad \left(\pi = \frac{n}{V}RT\right)$$

$$i = 1.83$$

$$\alpha = \frac{i-1}{n-1} = \frac{1.83-1}{2-1} = 0.83]$$

65. The vapour pressure of water at 100°C is 760 mm. What will be the vapour pressure at 95°C? The latent heat of water at this temperature range is 548 cal/g.

[**Ans.** 634.3 mm]

[**Hint:** Use Clausius-Clapeyron equation.

$$\log_{10}\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)]$$

66. Calculate the increase in vapour pressure of water per atmosphere rise in external pressure at 10°C. The vapour pressure of water at 10°C and 1 atm is equal to 9.2 mm.

[**Ans.** 0.1%]

[**Hint:** Use $\log_{10}\left(\dfrac{P_2}{P_1}\right) = \dfrac{V_l}{2.303RT}(P_2 - P_1)$

V_l = molar volume of liquid]

67. An aqueous solution of H_2SO_4 has density 1.84 g/mL. Solution contains 98% H_2SO_4 by mass. Calculate:

(i) molarity of solution
(ii) overall molarity of solution
(iii) molar volume
(iv) specific volume
(v) relative decrease in vapour pressure with respect to water, assuming H_2SO_4 as non-electrolyte at this high concentration.

[**Hint:** (i) $M = \dfrac{x \times d \times 10}{m_B}$

$$= \frac{98 \times 1.84 \times 10}{98} = 18.4$$

(ii) Weight of solution (1 litre) $= 1000 \times 1.84 = 1840$ g

$$w_B \text{ (weight of } H_2SO_4) = \frac{98}{100} \times 1840 = 1803.2 \text{ g}$$

$$w_A \text{ (weight of water)} = 1840 - 1803.2 = 36.8 \text{ g}$$

$$\text{Total number of moles} = \frac{w_A}{m_A} + \frac{w_B}{m_B} = \frac{36.8}{18} + \frac{1803.2}{98}$$
$$= 2.044 + 18.4 = 20.444$$

Overall molarity = 20.444

(iii) Molar volume $= \dfrac{\text{Volume}}{\text{Total moles}} = \dfrac{1000}{20.444}$

$$= 48.914 \text{ mL/mol}$$

(iv) Specific volume $= \dfrac{1}{\text{density}} = \dfrac{1}{1.84}$ mL/g $= 0.543$ mL/g

(v) Molality $(m) = \dfrac{w_B \times 1000}{m_B \times w_A} = \dfrac{98 \times 1000}{98 \times 2} = 500$

$$m = \frac{x_B \times 1000}{(1-x_B)\, m_A}$$

$$500 = \frac{x_B \times 1000}{(1-x_B) \times 18}$$

$$x_B = 0.9$$

According to Raoult's law: $\dfrac{\Delta p}{p_0} = x_B = 0.9$]

68. You are given two samples of HCl with molarity 0.341 and 0.143; volume of each sample being 1 litre. What will be the maximum volume of 0.243 *M* HCl that can be obtained by mixing the given samples in the following two conditions?
(i) When water is added for dilution.
(ii) When no water is added.

[**Ans.** (i) 2.0204 litre; (ii) 1.98 litre]

[**Hint:** (i) Let x litre of 0.341 M HCl and 1 litre of 0.143 M HCl be mixed to obtain 0.243 M HCl.

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$
$$0.341 \times x + 0.143 \times 1 = 0.243\ (1 + x)$$
$$(0.341 - 0.243)x = 0.243 - 0.143$$
$$0.098x = 0.1$$
$$x = 1.0204 \text{ litre}$$

Total volume = 1 + x = 2.0204 litre

Since, volume is greater than 2 litre, hence water is to be added.

(ii) Let x litre of 0.143 M HCl and 1 litre of 0.341 M HCl are mixed to obtain 0.243 M HCl.

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$
$$0.143 \times x + 0.341 \times 1 = 0.243(1 + x)$$
$$0.1x = 0.098$$
$$x = 0.98 \text{ litre}$$

Total volume = 1 + x = 1.98 litre

Since, volume is less than two litres, no water is to be added.]

69. What is the vapour pressure of a solution of glucose which has an osmotic pressure of 3 atmosphere at 20° C? The vapour pressure of water at 20° C is 17.39 mm. Consider the density of solution equal to that of solvent.

[**Ans.** 17.35 mm]

[**Hint:** Use: $\frac{\Delta p}{p_0} = \frac{\pi m}{dRT}$]

70. The osmotic pressure of an aqueous solution of a non-electrolyte is 18.8 atm at 15° C. What will be the vapour pressure of this solution at 100° C (Density of water at 100° C ≈ 1 g/cc)?

[**Ans.** 0.958 atm]

[**Hint:** Use, $\frac{\pi_1}{T_1} = \frac{\pi_2}{T_2}$ to calculate osmotic pressure at 100°C.

$$\frac{18.8}{278} = \frac{\pi_2}{373}$$
$$\pi_2 = 25.224 \text{ atm}$$

Use, $\frac{p_0 - p}{p_0} = \frac{\pi m}{dRT}$

$$\frac{1 - p}{1} = \frac{25.224 \times 18}{(1 \times 10^3) \times 0.0821 \times 373}$$
$$p = 0.958 \text{ atm}]$$

71. Calculate the osmotic pressure at 25° C of a solution containing 1 g of glucose and 1 g of sucrose in 1 litre of solution.

If it were not known that the solute was a mixture of glucose and sucrose, what would be the molecular weight of solute corresponding to the calculated osmotic pressure?

[**Ans.** 0.207 atm, 236.384]

[**Hint:** Use; $\pi V = (n_1 + n_2)RT$ to calculate osmotic pressure

$$\pi \times 1 = \left(\frac{1}{180} + \frac{1}{342}\right) \times 0.0821 \times 298$$
$$= 0.207 \text{ atm}$$

Use; $\pi V = \frac{w}{m} RT$ to calculate molar mass of solute.

$$0.207 \times 1 = \frac{2}{m} \times 0.0821 \times 298$$
$$m = 236.384]$$

72. 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. Calculate the osmotic pressure of mixture.

[**Ans.** 1.68 atm]

[**Hint:** Use: $\pi_1V_1 + \pi_2V_2 = \pi_R(V_1 + V_2)$

$$\pi_R = \frac{\pi_1V_1 + \pi_2V_2}{V_1 + V_2}$$
$$= \frac{1.2 \times 100 + 2.4 \times 300}{500} = 1.68 \text{ atm}]$$

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. A solution is defined as a:

(a) homogeneous mixture of two or more substances

(b) heterogeneous mixture of two or more substances

(c) homogeneous mixture of liquid and solid components only

(d) homogeneous mixture consisting of water as one of the components

2. Ideal solution is formed when its components:

(a) have zero heat of mixing only

(b) have zero volume change on mixing only

(c) have zero heat of mixing and zero volume change

(d) can be converted into gases

3. Solutions which distil without change in composition or temperature are called:

(a) amorphous (b) azeotropic mixture

(c) supersaturated (d) ideal

4. Azeotropic mixtures are:

(a) mixture of two solids

(b) those which boil at different temperatures

(c) those which can be fractionally distilled

(d) constant boiling mixtures

5. The solubility of a gas in a liquid is directly proportional to the pressure of the gas. This statement is:

(a) Raoult's law (b) Henry's law

(c) van't Hoff's law (d) None of these

6. Which of the following is not correct for an ideal solution?

(a) Raoult's law is obeyed for entire concentration range and temperatures

(b) $\Delta H_{\text{mix}} = 0$

(c) $\Delta V_{\text{mix}} = 0$

(d) $\Delta S_{\text{mix}} = 0$

7. The solubility of a gas in liquid increases with:
(a) increase in temperature
(b) reduction of gas pressure
(c) decrease in temperature and increase of gas pressure
(d) amount of liquid taken

8. Saturated solution of NaCl on heating becomes:
(a) supersaturated (b) unsaturated
(c) remains saturated (d) none of these

9. A supersaturated solution is a metastable solution whose concentration:
(a) is equal to the solubility of the substance in solvent
(b) is less than the solubility
(c) exceeds the solubility
(d) continuously changes

10. When a crystal of a solute is introduced into a supersaturated solution of the solute:
(a) the solute dissolves
(b) the solution becomes unsaturated
(c) the solution remains supersaturated
(d) the excess of solute crystallises out

11. An electrolyte dissolves in water if:
(a) lattice energy is less than hydration energy
(b) lattice energy is greater than hydration energy
(c) lattice energy is equal to hydration energy
(d) dissolution is endothermic

12. The solubility of a substance is defined as the amount of solute in grams:
(a) present in 100 g of the solvent
(b) present in 100 g of the solution
(c) present in 100 mL of the solution
(d) present in 1 litre of the solution

13. Which of the following will form an ideal solution?
(a) C_2H_5OH and water (b) HNO_3 and water
(c) $CHCl_3$ and CH_3COCH_3 (d) C_6H_6 and $C_6H_5CH_3$

14. Which of the following shows positive deviation from Raoult's law?
(a) C_6H_6 and $C_6H_5CH_3$ (b) C_6H_6 and CCl_4
(c) $CHCl_3$ and C_2H_5OH (d) $CHCl_3$ and CH_3COCH_3

15. Which of the following shows negative deviation from Raoult's law?
(a) $CHCl_3$ and acetone (b) C_6H_6 and C_2H_5OH
(c) $C_6H_5CH_3$ and C_6H_6 (d) C_6H_6 and CCl_4

16. An azeotropic mixture of two liquids boils at a lower temperature than either of them when:
(a) it is saturated
(b) it does not deviate from Raoult's law
(c) it shows negative deviation from Raoult's law
(d) it shows positive deviation from Raoult's law

17. A maxima or minima obtained in the temperature composition curve of a mixture of two liquids indicates:
(a) an azeotropic mixture
(b) an eutectic formation
(c) that the liquids are immiscible with one another
(d) that the liquids are partially miscible at the maximum or minimum

18. Among the following, that does not form an ideal solution is:
(a) C_6H_6 and $C_6H_5CH_3$ (b) C_2H_5Cl and C_2H_5OH
(c) C_6H_5Cl and C_6H_5Br (d) C_2H_5Br and C_2H_5I

19. Which of the following solution pairs can be separated by fractional distillation?
(a) Water-HNO_3 (b) Water-HCl
(c) Benzene-toluene (d) C_2H_5OH-water

20. When two liquids A and B are mixed, their boiling points become greater than both of them. The mixture is:
(a) ideal solution
(b) non-ideal solution with negative deviation from Raoult's law
(c) non-ideal solution with positive deviation from Raoult's law
(d) normal solution

21. The azeotropic mixture of water (b.pt. 100° C) and HCl (b.pt. 85° C) boils at 108.5 °C. When this mixture is distilled, it is possible to obtain:
(a) pure HCl
(b) pure water
(c) pure water as well as HCl
(d) neither HCl nor H_2O in their pure states

22. Pressure cooker reduces cooking time because:(CPMT 1990)
(a) the heat is more evenly distributed inside the cooker
(b) a large flame is used
(c) boiling point of water is elevated
(d) whole matter is converted into steam

23. A molal solution is one that contains one mole of a solute in:
(a) 1000 g of the solvent (b) one litre of the solution
(c) one litre of the solvent (d) 22.4 litre of the solution

24. In which mode of expression, the concentration of the solution remains independent of temperature?
(a) Normality (b) Molality (c) Molarity (d) Formality

25. 8 g NaOH is dissolved in one litre of solution. Its molarity is:
(a) $0.8\,M$ (b) $0.4\,M$ (c) $0.2\,M$ (d) $0.1\,M$

26. If 18 g of glucose is present in 1000 g of solvent, the solution is said to be:
(a) 1 molar (b) 0.1 molar (c) 0.5 molal (d) 0.1 molal

27. The molarity of pure water is: [CMC (Vellore) 1991]
(a) $100\,M$ (b) $55.6\,M$ (c) $50\,M$ (d) $18\,M$

28. For preparing $0.1\,M$ solution of H_2SO_4 in one litre, we need H_2SO_4:
(a) 9.8 g (b) 4.9 g (c) 49.0 g (d) 0.98 g

29. Mole fraction of $C_3H_5(OH)_3$ in a solution of 36 g of water and 46 g of glycerine is: (CPMT 1991)
(a) 0.46 (b) 0.36 (c) 0.20 (d) 0.40

30. H_2O_2 solution used for hair bleaching is sold as a solution of approximately 5.0 g H_2O_2 per 100 mL of the solution. The molecular mass of H_2O_2 is 34. The molarity of this solution is approximately:
(a) $0.15\,M$ (b) $1.5\,M$ (c) $3.0\,M$ (d) $3.4\,M$

31. The number of moles of solute per kg of a solvent is called its:
(a) molarity (b) normality
(c) mole fraction (d) molality

32. 1000 g aqueous solution of $CaCO_3$ contains 10 g of calcium carbonate. Concentration of the solution is:

(a) 10 ppm (b) 100 ppm
(c) 1000 ppm (d) 10000 ppm

33. A solution of $CaCl_2$ is 0.5 mol/litre; then the moles of chloride ion in 500 mL will be:
(a) 0.5 (b) 0.25 (c) 1.0 (d) 0.75

34. If 5.85 g of NaCl are dissolved in 90 g of water, the mole fraction of solute is: [CMC (Vellore) 1991]
(a) 0.0196 (b) 0.01 (c) 0.1 (d) 0.2

35. What is the normality of 1 M H_3PO_4 solution? (AIIMS 1991)
(a) 0.5 N (b) 1.0 N
(c) 2.0 N (d) 3.0 N

36. The molarity of a 0.2 N Na_2CO_3 solution will be:
(a) 0.05 M (b) 0.2 M
(c) 0.1 M (d) 0.4 M

37. How many grams of H_2SO_4 are present in 0.25 g mole of H_2SO_4? (CPMT 1990)
(a) 2.45 (b) 24.5 (c) 0.25 (d) 0.245

38. Colligative properties of the solution depend upon:
(a) nature of the solution (b) nature of the solvent
(c) number of solute particles (d) number of moles of solvent

39. Which of the following is a colligative property? (AFMC 2009)
(a) Surface tension (b) Osmotic pressure
(c) Optical rotation (d) Viscosity

40. Which is not a colligative property?
(a) Osmotic pressure
(b) Lowering in vapour pressure
(c) Depression in freezing point
(d) Refractive index

41. Colligative properties are applicable to:
(a) ideal dilute solutions (b) concentrated solutions
(c) non-ideal solutions (d) all of these

42. The vapour pressure of a solution having solid as solute and liquid as solvent is: [PET (MP) 2004]
(a) directly proportional to mole fraction of the solvent
(b) inversely proportional to mole fraction of the solvent
(c) directly proportional to mole fraction of the solute
(d) inversely proportional to mole fraction of the solute

43. If p_0 and p are the vapour pressures of a solvent and its solution respectively and N_1 and N_2 are the mole fractions of the solvent and solute respectively, then correct relation is:
(a) $p = p_0 N_2$ (b) $p = p_0 N_1$
(c) $p_0 = pN_1$ (d) $p = p_0(N_1/N_2)$

44. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressure of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively vapour pressure of the solution obtained by mixing 25 g of heptane and 35 g of octane will be : (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1}) (AIEEE 2010)
(a) 96.2 kPa (b) 144.5 kPa
(c) 72 kPa (d) 36.1 kPa

[Hint: Heptane A, $n_A = \frac{25}{100} = 0.25$

Octane $B, n_B = \frac{35}{114} = 0.31$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{0.25}{0.25+0.31} = 0.45$$
$$x_B = 0.55$$
$$p = p_A^0 x_A + p_B^0 x_B$$
$$= 105 \times 0.45 + 45 \times 0.55$$
$$= 72 \text{ kPa}]$$

45. The vapour pressure of water at room temperature is 30 mm of Hg. If the mole fraction of the water is 0.9, the vapour pressure of the solution will be:
(a) 30 mm of Hg (b) 24 mm of Hg
(c) 21 mm of Hg (d) 27 mm of Hg

46. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be: (AIEEE 2007)
(a) 360 (b) 350
(c) 300 (d) 700

47. When a non-volatile solute is dissolved in a solvent, the relative lowering in vapour pressure is equal to: [AFMC 2004; PMT (Himachal) 2006]
(a) mole fraction of solvent
(b) mole fraction of solute
(c) concentration of solute in g L^{-1}
(d) concentration of solute in g per 100 mL

48. The vapour pressure of a dilute aqueous solution of glucose is 750 mm of mercury at 373 K. The mole fraction of solute is:
(a) $\frac{1}{10}$ (b) $\frac{1}{7.6}$ (c) $\frac{1}{35}$ (d) $\frac{1}{76}$

[Hint: $\frac{p - p_s}{p}$ = Mole fraction of solute

p = Vapour pressure of water at 373 K is 760 mm]

49. The vapour pressure of a pure liquid 'A' is 70 torr at 27 °C. It forms an ideal solution with another liquid B. The mole fraction of B is 0.2 and total pressure of the solution is 84 torr at 27 °C. The vapour pressure of pure liquid B at 27 °C is: [CET (Karnataka) 2009]
(a) 14 torr (b) 56 torr (c) 140 torr (d) 70 torr

[Hint: $p_A = (1 - 0.2) \times 70 = 0.8 \times 70 = 56$ torr

$p_B = 84 - 56 = 28$ torr

$28 = 0.2 \times p_B^0$ or $p_B^0 = 140$ torr]

50. 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

51. 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

52. If the various terms in the following expressions have usual meanings, the van't Hoff factor 'i' cannot be calculated by which of the following expression?

(a) $\pi V = \sqrt{i}\,nRT$

(b) $\Delta T_f = i \times K_f \times m$

(c) $\Delta T_b = i \times K_b \times m$

(d) $\dfrac{P^\circ_{\text{solvent}} - P_{\text{solution}}}{P^\circ_{\text{solvent}}} = i\left[\dfrac{n}{N+n}\right]$

53. Semipermeable membrane is that which permits the passage of: **(CPMT 1990)**

(a) solute molecules only

(b) solvent molecules only

(c) solvent and solute molecules both

(d) neither solute nor solvent molecules

54. Which inorganic precipitate acts as semipermeable membrane?

(a) Calcium sulphate (b) Barium oxalate

(c) Nickel phosphate (d) Copper ferrocyanide

55. During osmosis, flow of water through a semipermeable membrane is: **[CBSE (Medical) 2006]**

(a) from solution having higher concentration only

(b) from both sides of semipermeable membrane with equal flow rates

(c) from both sides of semipermeable membrane with unequal flow rates

(d) from solution having lower concentration only

56. At constant temperature, the osmotic pressure of a solution is:

(a) directly proportional to the concentration

(b) inversely proportional to the concentration

(c) directly proportional to the square of concentration

(d) directly proportional to the square root of concentration

57. Osmotic pressure observed when benzoic acid is dissolved in benzene, is less than that expected from theoretical considerations. This is because : **[MGIMS (Wardha) 2008]**

(a) benzoic acid is organic solute

(b) benzoic acid has higher molar mass than benzene

(c) benzoic acid gets associated in benzene

(d) benzoic acid gets dissociated in benzene

58. Blood cells do not shrink in blood because blood is: **[PMT (Med) 2007]**

(a) hypertonic (b) isotonic

(c) equimolar (d) hypotonic

59. Isotonic solutions have the same:

(a) density (b) molar concentration

(c) normality (d) strength

60. The osmotic pressure of solution increases if: **(CPMT 1991)**

(a) temperature is decreased

(b) concentration is decreased

(c) number of solute particles is increased

(d) volume is increased

61. The osmotic pressure of a 5% solution of cane sugar (molecular mass 342) at 15°C is:

(a) 3.46 atm (b) 3.64 atm (c) 4.0 atm (d) 2.45 atm

62. A solution has an osmotic pressure of 0.821 atm at 300 K. Its concentration would be: **(IIT 1990)**

(a) 0.66 M (b) 0.32 M (c) 0.066 M (d) 0.033 M

63. If 3 g of glucose (molecular mass 180) is dissolved in 60 g of water at 15°C, then the osmotic pressure of this solution will be:

(a) 0.34 atm (b) 0.65 atm (c) 6.57 atm (d) 5.57 atm

64. The relationship between the values of osmotic pressure of 0.1 M solutions of KNO_3 (P_1) and CH_3COOH (P_2) is:

(a) $P_1 = P_2$ (b) $P_2 > P_1$

(c) $\dfrac{P_1}{P_1 + P_2} = \dfrac{P_2}{P_1 + P_2}$ (d) $P_1 > P_2$

65. 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) $1.5P$ (b) P (c) $0.5P$ (d) $0.75P$

66. 1 molar solution of a non-volatile and non-electrolyte compound will produce an osmotic pressure .... at 0°C.

(a) 1 atm (b) 44.8 atm (c) 10.0 atm (d) 22.4 atm

67. If 0.1 M solution of glucose and 0.1 M urea solution are placed on two sides of a semipermeable membrane to equal heights, then it will be correct to say that: **(CBSE 1992)**

(a) there will be no net movement across the membrane

(b) glucose will flow towards urea solution

(c) urea will flow towards glucose solution

(d) water will flow from urea solution towards glucose solution

68. Which solution will exert highest osmotic pressure?

(a) 1 M glucose solution (b) 1 M urea solution

(c) 1 M alum solution (d) 1 M NaCl solution

69. 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 pressure

(d) None of the above

70. A 0.6% urea solution would be isotonic with: **[CET (Karnataka) 2009]**

(a) 0.1 M glucose solution (b) 0.1 M KCl solution

(c) 0.6% glucose solution (d) 0.6% NaCl solution

71. Which one of the following solutions will have highest osmotic pressure? (Assume that all the salts are equally dissociated.)

(a) 0.1 M $Al_2(SO_4)_3$

(b) 0.1 M $BaCl_2$

(c) 0.1 M Na_2SO_4

(d) The solution obtained by mixing equal volumes of (b) and (c)

72. The following solutions have equal concentrations. Which one will show minimum osmotic pressure?

(a) $BaCl_2$ (b) $AgNO_3$

(c) Na_2SO_4 (d) $(NH_4)_3PO_4$

73. A solution of a substance containing 1.05 g per 100 mL was found to be isotonic with 3% glucose solution. The molecular mass of the substance is:

(a) 31.5 (b) 6.3 (c) 630 (d) 63

74. The osmotic pressure of equimolar solutions of $BaCl_2$, NaCl and glucose will be in the order:

(a) glucose > NaCl > $BaCl_2$ (b) $BaCl_2$ > NaCl > glucose
(c) NaCl > $BaCl_2$ > glucose (d) NaCl > glucose > $BaCl_2$

75. At 25°C, the highest osmotic pressure is exhibited by 0.1 *M* solution of: **(CBSE 1994)**

(a) $CaCl_2$ (b) KCl (c) glucose (d) urea

76. The plant cell will shrink when placed in:

(a) water (b) a hypotonic solution
(c) a hypertonic solution (d) an isotonic solution

77. The osmotic pressure of a solution at 273 K is 2.5 atm. Its osmotic pressure at 546 K under similar conditions will be:

(a) 0.5 atm (b) 1.0 atm (c) 2.5 atm (d) 5.0 atm

78. Which one of the following pairs of solutions will be expected to be isotonic under the same temperature? **[CET (Gujarat) 2006; AMU (Medical) 2009]**

(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* $Ca(NO_3)_2$ and 0.1 *M* Na_2SO_4

79. An aqueous solution of methanol in water has vapour pressure:

(a) less than that of water (b) equal to that of water
(c) more than that of water (d) equal to that of methanol

80. An aqueous solution is 1 molal in KI. Which change will cause the vapour pressure of the solution to increase? **[CBSE (PMT) 2010]**

(a) Addition of NaCl (b) Addition of Na_2SO_4
(c) Addition of 1 molal KI (d) Addition of water

81. Osmotic pressure of a solution containing 0.1 mole of solute per litre at 273 K is (in atm):

(a) $\frac{0.1\times 273}{0.0821}$ (b) $\frac{0.1}{1}\times 0.0821\times 273$
(c) $\frac{1}{0.1}\times 0.0821\times 273$ (d) $\frac{0.1}{1}\times\frac{0.0821}{273}$

82. A solution of urea contains 8.6 g per litre. It is isotonic with a 5% solution of a non-volatile solute. The molecular mass of the solute will be:

(a) 349 (b) 34.9 (c) 3490 (d) 861

83. The hard shell of an egg was dissolved in HCl. The egg was then placed in a concentrated solution of NaCl. What will happen?

(a) The egg will shrink
(b) The egg will swell
(c) The egg will become harder
(d) There will be hardly any visible change

84. Blood has been found isotonic with:

(a) saturated solution of NaCl
(b) saturated solution of KCl
(c) saturated solution of 1 : 1 mixture of NaCl and KCl
(d) normal sodium chloride solution

85. When a solute is dissolved in a solvent:

(a) vapour pressure of the solvent is decreased
(b) freezing point of the solution becomes less than that of solvent
(c) boiling point of the solution becomes higher than that of solvent
(d) all are correct

86. The molal elevation constant is the ratio of the elevation in boiling point to:

(a) molarity (b) molality
(c) mole fraction of solute (d) mole fraction of solvent

87. In cold countries, ethylene glycol is added to water in the radiators of cars during winters. It results in:

(a) reducing viscosity (b) reducing specific heat
(c) reducing freezing point (d) reducing boiling point

88. The best colligative property used for the determination of molecular masses of polymers is:

(a) relative lowering in vapour pressure
(b) osmotic pressure
(c) elevation in boiling point
(d) depression in freezing point

89. Ebullioscopy is concerned with:

(a) osmotic pressure of a solution
(b) elevation of boiling point of a solution
(c) depression in freezing point of a solution
(d) relative lowering in vapour pressure of a solution

90. Cryoscopy is concerned with:

(a) osmotic pressure of a solution
(b) elevation of boiling point of a solution
(c) depression in freezing point of a solution
(d) relative lowering in vapour pressure of a solution

91. Molecular mass of a non-volatile solute can be determined by:

(a) Cryoscopic method (b) Victor-Meyer's method
(c) Graham's method (d) Duma's method

92. Beckmann's thermometer measures:

(a) boiling point of the solution
(b) freezing point of the solution
(c) any temperature
(d) elevation in boiling point or depression in freezing point

93. The freezing point of 1% of lead nitrate solution in water will be: **[UGET (Manipal) 2006]**

(a) 2°C (b) 1°C (c) 0°C (d) below 0°C

94. A solution of 1.25 g of non-electrolyte in 20 g of water freezes at 271.94 K. If K_f is 1.86 K kg mol^{-1} then molecular mass of the solute will be:

(a) 207.8 (b) 179.79 (c) 209.6 (d) 109.5

95. The ratio of the value of colligative property for KCl solution to that of sugar solution at the same concentration is nearly:

(a) 1 (b) 2 (c) 0.5 (d) 2.5

96. The freezing point order of the solution of glucose is:

(a) 10% > 3% > 2% > 1% (b) 1% > 2% > 3% > 10%
(c) 1% > 3% > 10% > 2% (d) 10% > 1% > 3% > 2%

97. Which one of the following solutions has the highest b.p.? **[UGET (Manipal) 2006]**

(a) 0.1 *M* NaCl (b) 0.1 *M* urea
(c) 0.1 *M* $BaCl_2$ (d) 0.1 *M* glucose

98. The freezing point of 1 molal NaCl solution assuming NaCl to be 100% dissociated in water is:

(a) − 1.86°C (b) − 3.72°C
(c) + 1.86°C (d) + 3.72°C

99. Which of the following 0.1 *M* aqueous solutions will have the lowest freezing point? **(MLNR 1990)**
(a) K_2SO_4 (b) NaCl (c) Urea (d) Glucose

100. The freezing point of a 0.05 molal solution of a non-electrolyte in water is: **(MLNR 1990)**
(a) − 1.86°C (b) − 0.93°C (c) − 0.093°C (d) 0.93°C

101. The freezing point of equimolal aqueous solution will be highest for: **(IIT 1990)**
(a) $C_6H_5NH_3Cl$ (b) $Ca(NO_3)_2$
(c) $La(NO_3)_3$ (d) $C_6H_{12}O_6$ (glucose)

102. Elevation in boiling point was 0.52°C when 6 g of a compound *X* was dissolved in 100 g of water. Molecular mass of the compound *X* is: (K_b for water is 0.52 per 1000 g of water.)
(a) 120 (b) 60 (c) 600 (d) 180

103. The molal freezing point constant for water is 1.86. If 342 g of cane sugar is dissolved in 1000 g of water, the solution will freeze at:
(a) 1.86°C (b) − 1.86°C (c) − 3.92°C (d) 3.92°C

104. The molal elevation constant of water is 0.51. The boiling point of 0.1 molal aqueous NaCl solution is nearly: **(IIT 1991)**
(a) 100.05°C (b) 100.1°C (c) 100.2°C (d) 101.0°C

105. The molal elevation of an unknown solution is equal to the molal elevation of 0.1 *M* solution of urea. The concentration of unknown solution is:
(a) 1 *M* (b) 0.01 *M* (c) 0.1 *M* (d) none of these

106. Benzoic acid dissolved in benzene will show a molecular mass of:
(a) 122 (b) 61 (c) 244 (d) 366

107. If the observed and normal osmotic pressures of a KCl solution are 5.85 and 3.20 atm, the degree of dissociation of KCl is:
(a) 1 (b) 0.082 (c) 0.82 (d) 0.28

108. 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

109. If the observed and normal osmotic pressures of 1% NaCl solution are 5.7 and 3.0 atm, the degree of dissociation of NaCl is:
(a) 0.9 (b) 1.0 (c) 0.57 (d) 0.3

110. Which one of the following salts would have the same value of the van't Hoff factor as that of $K_3Fe(CN)_6$? **(CBSE 1994)**
(a) $Al_2(SO_4)_3$ (b) NaCl
(c) Na_2SO_4 (d) $Al(NO_3)_3$

111. Equimolal solutions of *A* and *B* show depression in freezing point in the ratio of 2 : 1. *A* remains in normal state in solution. *B* will be in . . . state in solution.
(a) normal (b) associated
(c) hydrolysed (d) dissociated

112. The values of observed and calculated molecular mass of $Ca(NO_3)_2$ are 65.4 and 164 respectively. The degree of ionisation of the salt will be:
(a) 0.25 (b) 0.50 (c) 0.60 (d) 0.75

113. Which of the following compounds corresponds to van't Hoff factor to be equal to 2 in dilute solution?
(a) KCl (b) $BaCl_2$ (c) K_2SO_4 (d) $C_6H_{12}O_6$

114. A solution containing 3.3 g of a substance in 125 g of benzene (b.pt. = 80°C) boils at 80.66°C. If K_b for benzene is 3.28 K kg mol^{-1} the molecular mass of the substance will be: **(CPMT 1992)**
(a) 130.20 (b) 129.20 (c) 132.20 (d) 131.20

115. The elevation in boiling point of a solution of 10 g of a binary electrolyte (molecular mass 100) in 100 g 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) $\frac{\Delta T_b}{10}$

116. The molal freezing point constant for water is 1.86 K kg mol^{-1}. Therefore, the freezing point of 0.1 *M* NaCl solution in water is expected to be: **(MLNR 1994)**
(a) − 1.86°C (b) − 0.186°C (c) − 0.372°C (d) + 0.372°C

117. Equal volumes of $M/20$ urea solution and $M/20$ glucose solution are mixed. The mixture will have osmotic pressure:
(a) equal to either of the solution
(b) less than either of the solution
(c) higher than either of the solution
(d) zero

118. Assuming the salts to be unionised in solution, which of the following has highest osmotic pressure?
(a) 1% CsCl (b) 1% RbCl (c) 1% KCl (d) 1% NaCl

119. Pure benzene freezes at 5.3°C. A solution of 0.223 g of phenyl acetic acid ($C_6H_5CH_2COOH$) in 4.4 g of benzene (K_f = 5.12 K kg mol^{-1}) freezes at 4.47°C. From the observation one can conclude that: **(AFMC 2010)**
(a) phenyl acetic acid exists as such in benzene
(b) phenyl acetic acid undergoes partial ionization in benzene
(c) phenyl acetic acid undergoes complete ionization in benzene
(d) phenyl acetic acid dimerizes in benzene

120. The movement of solvent molecules from higher concentration to lower concentration through semipermeable membrane under pressure is termed:
(a) osmosis (b) reverse osmosis
(c) dialysis (d) diffusion

121. During depression of freezing point experiment, an equilibrium is established between the molecules of: **(EAMCET 2009)**
(a) liquid solvent and solid solvent
(b) liquid solute and solid solvent
(c) liquid solute and solid solute
(d) liquid solvent and solid solute

122. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to: **(IIT 1996)**
(a) ionisation of benzoic acid
(b) dimerization of benzoic acid
(c) trimerization of benzoic acid
(d) solvation of benzoic acid

123. If 0.15 g of a solute, dissolved in 15 g of solvent, increases the boiling point by 0.216° C over that of the pure solvent, the molecular mass of the substance is (Molal elevation constant for the solvent is 2.16): **(CBSE 1999)**

(a) 1.01 (b) 10
(c) 10.1 (d) 100

124. The vapour pressure of benzene at a certain temperature is 640 mm of Hg. A non-volatile and non-electrolytic solid, weighing 2.175 g, is added to 39.08 g of benzene. The vapour pressure of the solution is 600 mm of Hg. What is the molecular mass of the solid substance? **(CBSE 1999)**
(a) 49.50 (b) 59.6
(c) 69.5 (d) 79.8

125. A 5% solution of cane sugar (mol. mass = 342) is isotonic with 1% solution of a substance X. The molecular mass of X is: **(CBSE 1998)**
(a) 34.2 (b) 171.2
(c) 68.4 (d) 136.8

126. The vapour pressure of a solvent decreased by 10 mm of mercury when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent, if the decrease in the vapour pressure is to be 20 mm of mercury? **(CBSE 1998)**
(a) 0.8 (b) 0.6
(c) 0.4 (d) 0.2

[**Hint:** Mole fraction of solute $= \frac{\text{lowering in vapour pressure}}{\text{vapour pressure of solvent}}$

Comparing under the two conditions,

$$\frac{0.2}{\text{mole fraction of solute}} = \frac{10}{20}$$

or mole fraction of solute = 0.4

mole fraction of solvent = (1 − 0.4) = 0.6]

127. Which of the following 0.10 m aqueous solution will have the lowest freezing point? **(CBSE 1997)**
(a) $Al_2(SO_4)_3$ (b) KI
(c) $C_6H_{12}O_6$ (d) $C_{12}H_{22}O_{11}$

128. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution? **(AIEEE 2009)**
(a) The solution formed is an ideal solution
(b) The solution is non-ideal, showing positive deviation from Raoult's law
(c) The solution is non-ideal, showing negative deviation from Raoult's law
(d) n-heptane shows positive deviation, while ethanol shows negative deviation from Raoult's law

129. X is a non-volatile solute and Y is volatile solvent. The following vapour pressures are obtained by dissolving X in Y.

X/mol L^{-1}	Y/mm Hg
0.1	P_1
0.25	P_2
0.01	P_3

The correct order of vapour pressure is : **[EAMCET (Engg.) 2010]**
(a) $P_1 < P_2 < P_3$ (b) $P_3 < P_2 < P_1$
(c) $P_3 < P_1 < P_2$ (d) $P_2 < P_1 < P_3$

130. 12.2 g of benzoic acid (M = 122) in 100 g water has elevation in boiling point of 0.27. $K_b = 0.54$ K kg mol^{-1}. If there is 100% polymerisation, the number of molecules of benzoic acid in associated state is:
(a) 1 (b) 2
(c) 3 (d) 4

131. For $[CrCl_3 \cdot xNH_3]$, elevation in boiling point of one molal solution is double of one molal solution of glucose; hence x is, if complex is 100% ionised:
(a) 4 (b) 5
(c) 6 (d) 3

132. If glycerol and methanol were sold at the same price in the market, which would be cheaper for preparing an antifreeze solution for the radiator of an automobile?
(a) Glycerol (b) Methanol
(c) Both are equal (d) None of these

133. Two liquids A and B have $P_A^0 : P_B^0 = 1:3$ 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

134. Relationship between osmotic pressure at 273 K when 1% glucose (π_1), 1% urea (π_2), 81% sucrose (π_3) are dissolved in 1 litre of water:
(a) $\pi_1 > \pi_2 > \pi_3$ (b) $\pi_2 > \pi_1 > \pi_3$
(c) $\pi_3 > \pi_1 > \pi_2$ (d) $\pi_1 = \pi_2 = \pi_3$

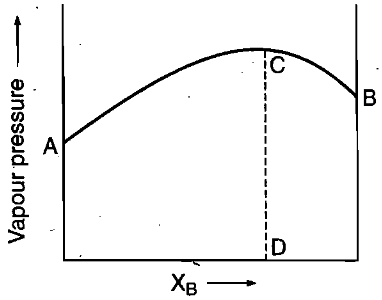
135. Which of the following property indicates weak intermolecular forces of attraction in liquid?
(a) High heat of vaporization (b) High vapour pressure
(c) High critical temperature (d) High boiling point

136. One mole of sugar is dissolved in two moles of water. The vapour pressure of the solution relative to that of pure water is:
(a) 2/3 (b) 1/3
(c) 3/2 (d) 1/2

137. The highest temperature at which vapour pressure of a liquid can be measured is:
(a) critical temperature (b) inversion temperature
(c) critical solu. temperature (d) b.pt. of liquid

138. The expression relating molality (m) and mole fraction (x_2) of solute in a solution is:
(a) $x_2 = \frac{mM_1}{1 + mM_1}$ (b) $x_2 = \frac{mM_1}{1 - mM_1}$
(c) $x_2 = \frac{1 + mM_1}{mM_1}$ (d) $x_2 = \frac{1 - mM_1}{mM_1}$

139. The diagram given below is a vapour pressure composition diagram for a binary solution of A and B.



In the solution, $A - B$ interactions are:
(a) similar to $A - A$ and $B - B$ interactions
(b) greater than $A - A$ and $B - B$ interactions
(c) smaller than $A - A$ and $B - B$ interactions
(d) unpredictable

140. The best and accurate method for determining osmotic pressure is: **(AFMC 1995)**
(a) negative pressure method
(b) Berkeley and Hartely method
(c) Morse and Frazer method
(d) Preffer's method

141. If all the following four compounds were sold at the same price, which would be cheapest for preparing an antifreeze solution for a car radiator? **(AMU 1997)**
(a) CH_3OH (b) C_2H_5OH
(c) $C_2H_4(OH)_2$ (d) $C_3H_5(OH)_3$

142. What is the osmotic pressure of the solution obtained by mixing 300 cm^3 of 2% (mass-volume) solution of urea with 300 cm^3 of 3.42% solution of sucrose of 20°C?
($R = 0.082$ L atm K^{-1} mol^{-1}) **(SCRA 2009)**
(a) 5 atm (b) 5.2 atm (c) 2.6 atm (d) 4.5 atm

[Hint : $\pi V = \left[\left(\frac{w_B}{m_B}\right)_{\text{urea}} + \left(\frac{w_B}{m_B}\right)_{\text{sucrose}}\right] RT$

$$\pi \times \frac{600}{1000} = \left[\frac{6}{60} + \frac{3 \times 3.42}{342}\right] 0.082 \times 293$$
$$\pi \times 0.6 = (0.1 + 0.03) \times 0.082 \times 293$$
$$\pi = 5.2 \text{ atm}]$$

143. A solution of 1 molal concentration of a solute will have maximum boiling point elevation when the solvent is: **[PMT (MP) 2000]**
(a) ethyl alcohol (b) acetone
(c) benzene (d) chloroform

144. Isotonic solutions have: **(DPMT 2000)**
(a) same boiling point (b) same vapour pressure
(c) same melting point (d) same osmotic pressure

145. The depressions in freezing point for 1 M urea, 1 M glucose and 1 M NaCl are in the ratio: **[CET (Haryana) 2000]**
(a) 1 : 2 : 3 (b) 3 : 2 : 2
(c) 1 : 1 : 2 (d) none of these

146. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is: **(IIT 2001)**
(a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL

147. The vapour pressure of a solvent A is 0.80 atm. When a non-volatile substance B is added to this solvent, its vapour pressure drops to 0.6 atm. The mole fraction of B in the solution is: **[PMT (MP) 2000]**
(a) 0.25 (b) 0.50 (c) 0.75 (d) 0.90

148. An aqueous solution of sucrose, $C_{12}H_{22}O_{11}$, containing 34.2 g/L has an osmotic pressure of 2.38 atmospheres at 17° C. For an aqueous solution of glucose, $C_6H_{12}O_6$, to be isotonic with this solution, it would have: **(AMU 1997)**
(a) 34.2 g/L (b) 17.1 g/L
(c) 18.0 g/L (d) 36.0 g/L of glucose

149. The molal b.pt. constant for water is 0.513° C kg mol^{-1}. When 0.1 mole of sugar is dissolved in 200 g of water, the solution boils under a pressure of 1 atm at: **(AIIMS 1991)**
(a) 100.513° C (b) 100.0513° C
(c) 100.256° C (d) 101.025° C

150. The correct expression relating molality (m), molarity (M), density (d) and molar mass (M_2) of a solute is:
(a) $m = \frac{M}{d + MM_2}$ (b) $m = \frac{M}{d - MM_2}$
(c) $m = \frac{d + MM_2}{M}$ (d) $m = \frac{d - MM_2}{M}$

151. The expression relating mole fraction of solute (x_2) and molarity (M) of the solution is:
(a) $x_2 = \frac{MM_1}{M(M_1 - M_2) + \rho}$ (b) $x_2 = \frac{MM_1}{M(M_1 - M_2) - \rho}$
(c) $x_2 = \frac{M(M_1 - M_2) + \rho}{MM_1}$ (d) $x_2 = \frac{M(M_1 - M_2) - \rho}{MM_1}$
(where ρ is the density of solution and M_1 and M_2 are the molar masses of solvent and solute, respectively.)

152. The boiling point of a solution of 0.11 g of a substance in 15 g of ether was found to be 0.1°C higher than that of pure ether. The molecular weight of the substance will be ($K_b = 2.16$) : **[PET (MP) 2002]**
(a) 148 (b) 158 (c) 168 (d) 178

153. 2.5 litre of 1 M NaOH solution are mixed with another 3 litre of 0.5 M NaOH solution. Then the molarity of the resulting solution is: **[CBSE (PMT) 2002]**
(a) 0.80 M (b) 1.0 M (c) 0.73 M (d) 0.50 M

154. In a mixture, 'A' and 'B' components show the negative deviations as: **(AIEEE 2002)**
(a) $\Delta V_{\text{mix}} > 0$
(b) $\Delta V_{\text{mix}} < 0$
(c) $A - B$ interaction is weaker than $A - A$ and $B - B$ interactions
(d) none of the above reasons is correct

155. A solution contains non-volatile solute of molecular mass M_2. Which of the following can be used to calculate the molecular mass of solute in terms of osmotic pressure? **[CBSE (PMT) 2002]**
(a) $M_2 = \frac{m_2}{\pi} VRT$ (b) $M_2 = \left(\frac{m_2}{V}\right)\frac{RT}{\pi}$
(c) $M_2 = \left(\frac{m_2}{V}\right)\pi RT$ (d) $M_2 = \left(\frac{m_2}{V}\right)\frac{\pi}{RT}$
(m_2 = mass of solute; V = volume of solution; π = osmotic pressure)

156. 0.6 g of an organic compound when dissolved in 21.7 g water freezes at 272.187 K. The molar mass of the organic compound is close to:
(K_f of water is 1.86 deg/molality; freezing point is 273 K) **(SCRA 2009)**
(a) 61 g mol^{-1} (b) 63 g mol^{-1}
(c) 65 g mol^{-1} (d) 67 g mol^{-1}

157. Osmotic pressure of urea solution at 10°C is 500 mm. Osmotic pressure of the solution becomes 105.3 mm, when it is diluted and temperature raised to 25°C. The extent dilution is: **[PMT (MP) 2004]**

(a) 8 times (b) 5 times (c) 4 times (d) 7 times

158. The average osmotic pressure of human blood is 7.8 bar at 37°C. What is the concentration of an aqueous NaCl solution that could be used in blood stream? **(AIIMS 2004)**

(a) 0.15 mol/L (b) 0.30 mol/L
(c) 0.45 mol/L (d) 0.60 mol/L

159. Camphor is often used in molecular mass determination because: **[CBSE-PMT (Pre.) 2004]**

(a) it is readily available
(b) it has very high cryoscopic constant
(c) it is volatile
(d) it is a solvent for organic substances

160. A 0.004 *M* solution of Na_2SO_4 is isotonic with a 0.010 *M* solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is: **[IIT (S) 2004]**

(a) 25% (b) 50% (c) 75% (d) 85%

161. Which of the following liquid pairs shows a positive deviation from Raoult's law? **[AIEEE 2004; AMU (Med) 2007]**

(a) Water-hydrochloric acid (b) Benzene-methanol
(c) Water-nitric acid (d) Acetone-chloroform

162. Which one of the following statements is false? **(AIEEE 2004)**

(a) Raoult's law states that vapour pressure of a component over a solution is proportional to mole fraction
(b) The osmotic pressure (π) of a solution is given by the relation $\pi = MRT$ where *M* is molarity of the solution
(c) The correct order of osmotic pressure for 0.01 *M* aqueous solution of each component is:

$$BaCl_2 > KCl > CH_3COOH > \text{Sucrose}$$

(d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

163. A solution of sucrose (molar mass = 342 g mol^{-1}) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be:
(K_f for water = 1.86 K kg mol^{-1}) **[CBSE (PMT) 2010]**

(a) –0.372°C (b) –0.520°C
(c) +0.372°C (d) –0.570°C

[Hint : $\Delta T = K_f \times \dfrac{w_B \times 1000}{m_B \times w_A}$

$= 1.86 \times \dfrac{68.5 \times 1000}{342 \times 1000}$

$= 0.372$

Freezing point of solution = 0 – 0.372°C
= –0.372°C]

164. Which of the following is incorrect? **[CET (J&K) 2005]**

(a) Relative lowering of vapour pressure is independent of the nature of the solute and the solvent
(b) The vapour pressure is a colligative property
(c) Vapour pressure of a solution is lower than that of the solvent
(d) The relative lowering of vapour pressure is directly proportional to the original pressure

165. Calculate the molal depression constant of a solvent which has freezing point 16.6°C and latent heat of fusion 180.75 J g^{-1}. **[JEE (Orissa) 2005]**

(a) 2.68 (b) 3.86 (c) 4.68 (d) 2.86

166. If for a sucrose solution, elevation in boiling point is 0.1°C then what will be the boiling point of NaCl solution for same molal concentration? **[BHU (Pre.) 2005]**

(a) 0.1°C (b) 0.2°C (c) 0.08°C (d) 0.01°C

167. Which has minimum osmotic pressure? **(DCE 2005)**

(a) 200 mL of 2 *M* NaCl solution
(b) 200 mL of 1 *M* glucose solution
(c) 200 mL of 2 *M* urea solution
(d) All have same

168. Solution *A* contains 7 g/L of $MgCl_2$ and solution *B* contains 7 g/L of NaCl. At room temperature, the osmotic pressure of: **(DCE 2005)**

(a) solution *A* is greater than *B*
(b) both have same osmotic pressure
(c) solution *B* is greater than *A*
(d) can't determine

169. The van't Hoff factor for $BaCl_2$ at 0.01 *M* concentration is 1.98. The percentage dissociation of $BaCl_2$ at this concentration is: **[PET (Kerala) 2005]**

(a) 49 (b) 69 (c) 89 (d) 98
(e) 100

170. Equimolar solutions in the same solvent have: **(AIEEE 2005)**

(a) same boiling point but different freezing points
(b) same freezing point but different boiling points
(c) same freezing and boiling points
(d) different freezing and boiling points

171. A solution of urea (mol. mass 56 g mol^{-1}) boils at 100.18°C at the atmospheric pressure. If K_f and K_b for water are 1.86 and 0.512 K kg mol^{-1} respectively, the above solution will freeze at: **[CBSE-PMT (Pre.) 2005]**

(a) 0.654°C (b) – 0.654°C
(c) 6.54°C (d) – 6.54°C

172. If 0.5 g of a solute (molar mass 100 g mol^{-1}) in 25 g of solvent elevates the boiling point by 1 K, the molar boiling point constant of the solvent is: **[PMT (Kerala) 2006]**

(a) 2 (b) 8 (c) 5 (d) 0.5
(e) 10

173. Osmotic pressure observed when benzoic acid is dissolved in benzene, is less than that expected from theoretical considerations. This is because: **[KCET 2006]**

(a) benzoic acid is an organic solute
(b) benzoic acid has higher molar mass than benzene
(c) benzoic acid gets associated in benzene
(d) benzoic acid gets dissociated in benzene

174. A 5% solution by mass of cane sugar in water has freezing point of 271 K and freezing point of pure water is 273.15 K. The freezing point of a 5% solution (by mass) of glucose in water is: **(AIIMS 2006)**

(a) 271 K (b) 273.15 K (c) 269.07 K (d) 277.23 K

[**Hint:** $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$$2.15 = K_f \times \frac{5 \times 1000}{342 \times 95} \quad \ldots\text{(i)} \quad \text{(for sucrose)}$$

$$\Delta T = K_f \times \frac{5 \times 1000}{180 \times 95} \quad \ldots\text{(ii)} \quad \text{(for glucose)}$$

Dividing eq. (i) by eq. (ii), we get,

$$\Delta T = 4.18 \text{ K}$$
$$T = T_0 - 4.18$$
$$= 273.15 - 4.18 = 269.07 \text{ K}]$$

175. 18 g glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is: **(AIEEE 2006)**

(a) 759 torr (b) 7.60 torr (c) 76 torr (d) 752.4 torr

176. Depression in freezing point is 6 K for NaCl solution. If K_f for water is 1.86 K/kg mol, amount of NaCl dissolved in 1 kg water is: **(DCE 2006)**

(a) 3.42 (b) 1.62 (c) 3.24 (d) 1.71

177. Observe the following observations:

π_{obs} = observed colligative property
π_{cal} = theoretical colligative property assuming normal behaviour of solute

van't Hoff factor (i) is given by: **[CET (J&K) 2006]**

(a) $i = \pi_{obs} \times \pi_{cal}$ (b) $i = \pi_{obs} + \pi_{cal}$
(c) $i = \pi_{obs} - \pi_{cal}$ (d) $i = \frac{\pi_{obs}}{\pi_{cal}}$

178. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1 g cm^{-3}, molar mass of the substance will be: **(AIEEE 2007)**

(a) 210.0 g mol^{-1} (b) 90.0 g mol^{-1}
(c) 115.0 g mol^{-1} (d) 105.0 g mol^{-1}

[**Hint:** For isotonic solutions:

$$\pi_1 = \pi_2 \quad \because \quad \pi = CRT$$
$$C_1 = C_2$$
$$\frac{1.5/60}{V} = \frac{5.25/m}{V}$$
$$\therefore \quad m = 210]$$

179. Concentrated aqueous sulphuric acid 98% H_2SO_4 by mass has a density of 1.80 g mL^{-1}. Volume of acid required to make one litre of 0.1M H_2SO_4 solution is: **[CBSE (Med) 2007]**

(a) 16.65 mL (b) 22.20 mL
(c) 5.55 mL (d) 11.10 mL

[**Hint:** $M = \frac{x \times d \times 10}{m_B} = \frac{98 \times 1.80 \times 10}{98} = 18$

$$M_1V_1 = M_2V_2$$
$$18 \times V_1 = 0.1 \times 1000$$
$$V_1 = \frac{100}{18} = 5.55 \text{ mL}]$$

180. If the vapour pressures of pure A and pure B at 298 K are 60 and 15 torr respectively, what would be the mole fraction of A in vapour phase (at this temperature) in a solution that contains 20 mole per cent of A in the $(A + B)$ binary mixture in the liquid phase? **(SCRA 2007)**

(a) 0.2 (b) 0.3
(c) 0.5 (d) 0.7

[**Hint:** $x_A = \frac{20}{100} = 0.2, \quad \therefore \quad x_B = 0.8$

$$p = p_A + p_B = p_A^0 x_A + p_B^0 x_B$$
$$= 60 \times 0.2 + 15 \times 0.8 = 12 + 12 = 24$$

Mole fraction of A in the vapour phase, *i.e.*, y_A may be calculated as:

$$p_A = y_A \times p$$
$$12 = y_A \times 24$$
$$y_A = \frac{12}{24} = 0.5]$$

181. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene ($K_f = 1.72$ kg mol^{-1}), a freezing point depression of 2K is observed. The van't Hoff factor (i) is: **(IIT 2007)**

(a) 0.5 (b) 1
(c) 2 (d) 3

[**Hint:** $\Delta T = i \times K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$$2 = i \times 1.72 \times \frac{20 \times 1000}{172 \times 50}$$
$$i = 0.5]$$

182. At 80°C, the vapour pressure of pure liquid A is 520 mm of Hg and that of pure liquid B is 1000 mm of Hg. If a mixture of solution A and B boils at 80°C and 1 atm pressure, the amount of A in the mixture is: (1 atm = 760 mm of Hg) **(AIEEE 2008)**

(a) 50 mol per cent (b) 52 mol per cent
(c) 34 mol per cent (d) 48 mol per cent

[**Hint :** $p = p_A^0 x_A + p_B^0 x_B$

$$760 = 520 \times x_A + 1000(1 - x_A)$$

$x_A = 0.50$, *i.e.*, 50 mol per cent.]

183. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of resulting solution will be : **(AIEEE 2008)**

(a) 17.325 mm Hg (b) 17.675 mm Hg
(c) 15.75 mm Hg (d) 16.5 mm Hg

[**Hint :** $p = p^0 x_A$

$$= 17.5 \times \frac{178.2/18}{178.2/18 + \frac{18}{180}}$$
$$= 17.325 \text{ mm Hg}]$$

184. Which of the following can be measured by the Ostwald-Walker dynamic method ? **(KCET 2008)**

(a) Vapour pressure of the solvent
(b) Relative lowering of vapour pressure
(c) Lowering of vapour pressure
(d) All of the above

185. Cryoscopic constant is the depression in freezing point produced by : **[Comed (Karnataka) 2008]**

(a) 1% solution (b) 1 molar solution
(c) 1 molal solution (d) 1 N solution

186. Which among the following gas will greatly deviate from Henry's law in water ? **[PMT (Kerala) 2008]**

(a) H_2 (b) N_2

(c) CH_4 (d) CO_2

(e) Ar

187. Vapour pressure increases with increase in : **[JEE (Orissa) 2008]**

(a) concentration of solution containing non-volatile solute

(b) temperature upto boiling point

(c) temperature upto triple point

(d) altitude of the concerned place of boiling

188. When mercuric iodide is added to the aqueous solution of potassium iodide: **[BHU (Mains) 2008]**

(a) freezing point is raised

(b) freezing point is lowered

(c) freezing point does not change

(d) boiling point is raised

[**Hint :** $2KI + HgI_2 \longrightarrow K_2[HgI_4]$

Number of particles decreases due to above reaction hence freezing point is raised.]

189. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from dissolved in 10 moles of water at 298 K and 5 atm pressure is: **(IIT 2009)**

(a) 4×10^{-4} (b) 4×10^{-5}

(c) 5×10^{-4} (d) 4×10^{-6}

[**Hint :** $p_{N_2} = x_{N_2} \times p_{\text{total}}$

$= 0.8\times5 = 4$ atm

According to Henry's law :

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

$$4 = 1\times10^5 \times \frac{n_{N_2}}{n_{N_2} \times n_{H_2O}}$$

$$\frac{n_{N_2} + n_{H_2O}}{n_{N_2}} = \frac{1\times10^5}{4}$$

$$\frac{n_{N_2} + 10}{n_{N_2}} = 0.25\times10^5$$

$$n_{N_2} = 4\times10^{-4}\,]$$

190. A 0.002 *m* aqueous solution of an ionic compound $Co(NH_3)_5(NO_2)Cl$ freezes at –0.00732°C. Number of moles of ions which 1 mol of ionic compound produces on being dissolved in water will be : ($K_f = -1.86$°C/m) **[CBSE (Med) 2009]**

(a) 1 (b) 2 (c) 3 (d) 4

[**Hint :** $\Delta T = i \times K_f \times m$

$$0.00732 = i \times 1.86 \times 0.002$$

$$i = 1.967 \approx 2\,]$$

191. A solution is separated from pure solvent by a semipermeable membrane at 298 K. The difference in the height of the solution and the solvent is 0.9 m. If K_f and freezing point of the solvent are 30 K kg mol^{-1} and 250.3 K, respectively, the temperature at which the solution freezes is: **(ISAT 2010)**

(a) 250.10 K (b) 250.25 K

(c) 250.20 K (d) 250.05 K

(Assume density of solution to be 1 g/cc)

[**Hint :** $\pi \times 13.6 \times g \times 76 = 90 \times g \times 1$

$$\pi = 0.087 \text{ atm}$$

$$\pi = CRT$$

$$0.087 = C \times 0.082 \times 298$$

$$C = 3.56\times10^{-3}\,M$$

$$\Delta T = K_f \times m$$

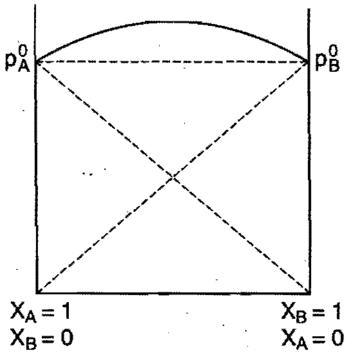
$$= 30 \times 3.56\times10^{-3} \simeq 0.1$$

∴ Freezing point of solution will be : 250.3 – 0.1

= 250.2 K]

Set-2: The questions given below may have more than one correct answers

1. The given graph indicates:



(a) (+) deviation (b) (–) deviation

(c) no deviation (d) none of these

2. Which is the correct statement?

(a) Minimum boiling azeotropic mixture boils at temperature lower than either of the two pure components

(b) Maximum boiling azeotropic mixture boils at temperature higher than either of the two pure components

(c) Minimum boiling azeotropic mixture shows (+)ve deviation

(d) Maximum boiling azeotropic mixture shows (–)ve deviation

3. A certain non-volatile substance (non-electrolyte) contains 40% C, 6.7% H, 53.3% O. An aqueous solution containing 5% by mass of the solute boils at 100.15° C. Molecular formula of the compound is:

(a) CH_2O (b) $C_2H_4O_2$

(c) $C_6H_{12}O_6$ (d) $C_{12}H_{22}O_{11}$

4. Difference between diffusion and osmosis is:

(a) a semipermeable membrane is required for osmosis while diffusion requires no semipermeable membrane

(b) in osmosis the movement of molecules is only in one direction whereas in diffusion movement is on both sides

(c) in osmosis only the solvent moves while in diffusion solute and solvent both move

(d) none of the above

5. For a non-volatile solute:

(a) vapour pressure of solute is zero

(b) vapour pressure of solution = vapour pressure of pure solvent

(c) vapour pressure of solution = vapour pressure of solvent in solution

(d) all of the above

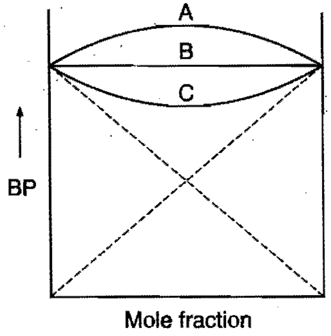
6. In which of the following cases does osmosis take place if the solutions are separated by a semipermeable membrane?
(a) 0.1 M NaCl and 0.2 M glucose
(b) 0.1 M sucrose and 0.1 M fructose
(c) 0.05 M $K_4[Fe(CN)_6]$ and 0.1 M $CaCl_2$
(d) 10^{-3} M $CaCl_2$ and 1.5×10^{-3} M NaCl

7. Match the following:

Solute (equimolar)	**π (OP) ratio**
(i) Urea, glucose, fructose	(A) 1 : 0.8 : 1
(ii) NaCl, $MgCl_2$, K_2SO_4	(B) 1 : 2 : 3
(iii) $Al_2(SO_4)_3$, Na_3PO_4, $K_4Fe(CN_6)$	(C) 1 : 1 : 1
(iv) Glucose, NaCl, $CaCl_2$	(D) 2 : 3 : 3

	(i)	(ii)	(iii)	(iv)
(a)	A	B	C	D
(b)	B	D	C	A
(c)	D	B	A	C
(d)	C	D	A	B

8. Match the following graph:



A (i) (+) deviation
B (ii) Ideal
C (iii) (–) deviation
(a) (A) (i), (B) (ii), (C) (iii)
(b) (A) (iii), (B) (ii), (C) (i)
(c) (A) (ii), (B) (iii), (C) (i)
(d) none of these

9. Vapour pressure of methyl alcohol and ethyl alcohol solutions is represented by $P = 115x_A + 140$ where x_A is the mole fraction of methyl alcohol. The value of $\lim\limits_{x_A \to 0} \frac{P_B^0}{x_B}$ is:
(a) 255 (b) 115
(c) 140 (d) 135

10. To 10 mL of 1 M $BaCl_2$ solution 5 mL of 0.5 M K_2SO_4 is added, $BaSO_4$ is precipitated out. What will happen?
(a) F.pt. is increased (b) B.pt. is increased
(c) F.pt. is lowered (d) B.pt. is lowered

11. Which is a dimensionless quantity?
(a) Mole fraction (b) Molality
(c) % by wt. of solvent (d) % by wt. of solution

12. Which of the following concentration terms is/are independent of temperature? **[PET (Kerala) 2006; CET (Gujarat) 2006; DCE 2007]**
(a) Molarity
(b) Molarity and mole fraction
(c) Mole fraction and molality
(d) Molality and normality
(e) Only molality

13. In the depression of freezing point experiment, it is found that: **(IIT 1999)**
(a) the vapour pressure of the solution is less than that of pure solvent
(b) the vapour pressure of solution is more than that of pure solvent
(c) only solute molecules solidify at the freezing point
(d) only solvent molecules solidify at the freezing point

14. Which of the following is/are correct for a solution of a particular concentration?
(a) Molarity is always less than molality
(b) Formality is equivalent to molarity
(c) Mole fraction is equivalent to mass fraction
(d) Normality of H_2SO_4 solution is double than its molarity

15. Effect of adding a non-volatile solute to a solvent is:
(a) to lower the vapour pressure
(b) to increase its freezing point
(c) to increase its boiling point
(d) to decrease its osmotic pressure

16. Which of the following form/s an ideal solution?
(a) Ethyl bromide + ethyl iodide
(b) Ethyl alcohol + water
(c) Chloroform + benzene
(d) Benzene + toluene

17. Osmotic pressure of a solution is:
(a) directly proportional to the molar concentration of the solution
(b) inversely proportional to the molecular weight of the solute
(c) inversely proportional to the temperature
(d) directly proportional to the volume of the solution

18. Which of the following is/are true?
(a) For the same solution, elevation in boiling point = depression in freezing point
(b) van't Hoff factor for a dilute solution of $BaCl_2$ is 3
(c) Elevation in boiling point is due to increase in vapour pressure
(d) Depression in freezing point is due to decrease in vapour pressure

19. In the following question, more than one of the answers given may be correct. Select correct answer and mark it according to the code : **[BHU (Mains) 2008]**
A solution containing components A and B exhibits positive deviation from Raoult's law only when

(1) $\Delta V_{\text{mixing}} = +\text{ve}$

(2) $\Delta H_{\text{mixing}} = -\text{ve}$

(3) $A - B$ attraction forces < $A - A$ and $B - B$ attraction forces

(4) $A - B$ attraction forces > $A - A$ and $B - B$ attraction forces

Codes:

(a) 1, 2 and 3 are correct

(b) 1 and 2 are correct

(c) 2 and 4 are correct

(d) 1 and 3 are correct

20. Consider the following statements in respect of an ideal solution:

1. Raoult's law is valid for an ideal solution over the whole concentration range
2. Enthalpy of mixing is zero, *i.e.*, $\Delta H_{\text{mix}} = 0$
3. Volume of mixing is not zero, *i.e.*, $\Delta V_{\text{mix}} \neq 0$
4. The components of ideal solution cannot be separated by fractional distillation.

Which of the statements given above is/are correct? **(SCRA 2009)**

(a) 3 and 4 (b) 1 and 4

(c) 1 and 2 (d) 2 and 3

21. Consider the following :

At constant pressure, boiling point of a solution is greater than the boiling point of its pure liquid solvent because

1. Solute is non-electrolyte
2. Solute is involatile
3. Chemical potential of solvent in solution is less than the chemical potential of solvent in its pure state at constant pressure

Which of the above are correct? **(SCRA 2009)**

(a) 1, 2 and 3 (b) 1 and 2 only

(c) 1 and 3 only (d) 2 and 3 only

22. Which values can be obtained from the information represented by the vapour pressure curve of a liquid?

1. Normal boiling point
2. Normal freezing point
3. Enthalpy of vaporisation **(DUMET 2010)**

(a) 1 only (b) 1 and 2 only

(c) 1 and 3 only (d) 1, 2 and 3

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as '**Assertion**' **(A)** and '**Reason**' **(R).** While answering these questions you are required to choose any one of the following four options:

(a) If both (A) and (R) are correct and (R) is the correct explanation for (A).

(b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).

(c) If (A) is correct but (R) is incorrect.

(d) If (A) is incorrect but (R) is correct.

1. (A) The dissolution of gases in water is always an endothermic process.
(R) Dissolution of gases in water proceed with negative value of ΔS.

2. (A) Water boiling at 100°C at 1 atmospheric pressure in a beaker is not at equilibrium.
(R) It refers to an open system.

3. (A) A solution which contains one gram equivalent of solute per litre of the solution is called a normal solution.
(R) A normal solution means a solution in which the solute does not associate or dissociate.

4. (A) The sum of mole fractions of all the components of a solution is unity.
(R) Mole fraction is a temperature dependent quantity.

5. (A) Iodine is more soluble in CCl_4 than in water.
(R) Non-polar solutes are more soluble in non-polar solvents.

6. (A) Vapour pressure of 0.5 M sugar solution is more than 0.5 M KCl solution.
(R) Lowering of vapour pressure is directly proportional to the number of species present in the solution.

7. (A) Non-ideal solutions form azeotropic mixture.
(R) Boiling point of azeotropic mixture is higher than boiling points of its both components.

8. (A) One molar solution is always more concentrated than one molal solution.
(R) The amount of solvent in 1 M and 1 m aqueous solution is not equal.

9. (A) Camphor is used as solvent in the determination of molecular mass of naphthalene and anthracene etc.
(R) Camphor has high molal elevation constant.

10. (A) 0.1 M solution of glucose has same increment in freezing point than 0.1 M solution of urea.
(R) K_f for both has different values. **(AIIMS 1997)**

11. (A) Molarity of 0.02 N solution of HNO_3 is 0.02 M.
(R) Molarity and normality of a solution are never equal.

12. (A) Larger the value of cryoscopic constant of the solvent, lesser will be the freezing point of the solution.
(R) Depression in the freezing point depends on the nature of the solvent.

13. (A) 0.1 M solution of NaCl has greater osmotic pressure than 0.1 M solution of glucose at same temperature.
(R) In solution, NaCl dissociates to produce more number of particles.

14. (A) Henry's law and Raoult's law are not independent, *i.e.*, one can be derived from the other.
(R) The partial pressure is directly proportional to the mole fraction of the concerned species for ideal solutions.

15. (A) The water pouch of instant cold pack for treating athletic injuries breaks when squeezed and NH_4NO_3 dissolves thus lowering the temperature.
(R) Addition of non-volatile solute into solvent results into depression of freezing point of solvent. **(AIIMS 2006)**

16. (A) In a pressure cooker, the water is brought to boil. The cooker is then removed from the stove. Now on removing the lid of pressure cooker, the water starts boiling again.
(R) The impurities in water bring down its boiling point.
[**Hint:** In pressure cooker, water boils above 100° C. When the lid of cooker is opened, pressure is lowered so that boiling point decreases and water boils again.]

17. (A) An increase in surface area increases the rate of evaporation.
(R) Stronger the inter-molecular attractive forces, faster is the rate of evaporation at a given temperature.

18. (A) An ideal solution obeys Raoult's law.
(R) In an ideal solution, solute-solute as well as solvent-solvent interactions are similar to solute-solvent interaction.

Answers : OBJECTIVE QUESTIONS

Set–1

1. (a) 2. (c) 3. (b) 4. (d) 5. (b) 6. (d) 7. (c) 8. (b)
9. (c) 10. (d) 11. (a) 12. (a) 13. (d) 14. (c) 15. (a) 16. (d)
17. (a) 18. (b) 19. (c) 20. (b) 21. (d) 22. (c) 23. (a) 24. (b)
25. (c) 26. (d) 27. (b) 28. (a) 29. (c) 30. (b) 31. (d) 32. (d)
33. (b) 34. (a) 35. (d) 36. (c) 37. (b) 38. (c) 39. (b) 40. (d)
41. (a) 42. (a) 43. (b) 44. (c) 45. (d) 46. (b) 47. (b) 48. (d)
49. (c) 50. (c) 51. (b) 52. (a) 53. (b) 54. (d) 55. (d) 56. (a)
57. (c) 58. (b) 59. (b) 60. (c) 61. (a) 62. (d) 63. (c) 64. (d)
65. (a) 66. (d) 67. (a) 68. (c) 69. (b) 70. (c) 71. (a) 72. (b)
73. (d) 74. (b) 75. (a) 76. (c) 77. (d) 78. (d) 79. (a) 80. (d)
81. (b) 82. (a) 83. (a) 84. (d) 85. (d) 86. (b) 87. (c) 88. (b)
89. (b) 90. (c) 91. (a) 92. (d) 93. (d) 94. (d) 95. (b) 96. (b)
97. (c) 98. (b) 99. (a) 100. (c) 101. (d) 102. (b) 103. (b) 104. (b)
105. (c) 106. (c) 107. (c) 108. (a) 109. (a) 110. (d) 111. (b) 112. (d)
113. (a) 114. (d) 115. (a) 116. (c) 117. (a) 118. (d) 119. (d) 120. (b)
121. (a) 122. (b) 123. (d) 124. (c) 125. (c) 126. (b) 127. (a) 128. (b)
129. (d) 130. (b) 131. (a) 132. (b) 133. (a) 134. (b) 135. (b) 136. (a)
137. (d) 138. (c) 139. (c) 140. (b) 141. (a) 142. (b) 143. (c) 144. (d)
145. (c) 146. (a) 147. (a) 148. (c) 149. (c) 150. (b) 151. (a) 152. (b)
153. (c) 154. (b) 155. (b) 156. (b) 157. (b) 158. (b) 159. (b) 160. (c)
161. (b) 162. (d) 163. (a) 164. (d) 165. (b) 166. (b) 167. (b) 168. (a)
169. (a) 170. (d) 171. (b) 172. (c) 173. (c) 174. (c) 175. (d) 176. (b)
177. (d) 178. (a) 179. (c) 180. (c) 181. (a) 182. (a) 183. (a) 184. (b)
185. (c) 186. (d) 187. (b) 188. (a) 189. (a) 190. (b) 191. (c)

Set–2

1. (a) 2. (a, b, c, d) 3. (c) 4. (a, b, c) 5. (a, c) 6. (c) 7. (d) 8. (b)
9. (c) 10. (b, c) 11. (a, c, d) 12. (c) 13. (a, d) 14. (b, d) 15. (a, c) 16. (a, d)
17. (a, d) 18. (b, d) 19. (d) 20. (c) 21. (d) 22. (b)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (d) 2. (a) 3. (c) 4. (c) 5. (a) 6. (a) 7. (c) 8. (d)
9. (a) 10. (c) 11. (c) 12. (a) 13. (a) 14. (b) 15. (a) 16. (c)
17. (c) 18. (a)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

The following questions contain single correct option:

1. Three solutions of HCl having normality 12 *N*, 6 *N* and 2 *N* are mixed to obtain a solution of 4 *N* normality. Which among the following volume ratio is correct for the above three components?

(a) 1 : 1 : 5 (b) 1 : 2 : 6 (c) 2 : 1 : 9 (d) 1 : 2 : 4

[Hint: $N_1V_1 + N_2V_2 + N_3V_3 = N_R(V_1 + V_2 + V_3)$

$12 \times 1 + 6 \times 2 + 2 \times 6 = N_R(9)$

$N_R = 4$]

2. 6.8 g H_2O_2 is dissolved in 224 mL solution. This solution will be labelled as:

(a) 0.224 V (b) 20 V (c) 5 V (d) 10 V

[Hint: $M = \frac{w_B \times 1000}{m_B \times V} = \frac{6.8}{34} \times \frac{1000}{224}$

$= \frac{200}{224}$

Volume strength $V = M \times 11.2$

$= \frac{200}{224} \times 11.2 = 10$]

3. A solution weighing *a* g has molality *b*. The molecular mass of solute if the mass of solute is *c* g, will be:

(a) $\frac{c}{b} \times \frac{1000}{(a-c)}$ (b) $\frac{b}{a} \times \frac{1000}{(a-b)}$

(c) $\frac{b}{c} \times \frac{1000}{(a-c)}$ (d) $\frac{c}{a} \times \frac{1000}{(b-a)}$

[Hint: Molality, $m = \frac{w_B}{m_B} \times \frac{1000}{w_A}$

$b = \frac{c}{m_B} \times \frac{1000}{(a-c)}$

$m_B = \frac{c}{b} \times \frac{1000}{(a-c)}$]

4. Two solutions of H_2SO_4 of molarities *x* and *y* are mixed in the ratio of V_1 mL : V_2 mL to form a solution of molarity M_1. If they are mixed in the ratio of V_2 mL : V_1 mL, they form a solution of molarity M_2. Given $V_1 / V_2 = \frac{x}{y} > 1$ and $\frac{M_1}{M_2} = \frac{5}{4}$, then *x* : *y* is:

(a) 2 : 1 (b) 4 : 1 (c) 1 : 2 (d) 3 : 1

[Hint: Molarity of the mixture can be calculated as:

$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$

where, M_R = resultant solution

$V_1 \times x + V_2 \times y = M_1(V_1 + V_2)$ ... (i)

$V_2 \times x + V_1 \times y = M_2(V_1 + V_2)$ ... (ii)

Dividing eq. (i) by eq. (ii), we get

$$\frac{V_1x + V_2y}{V_2x + V_1y} = \frac{M_1}{M_2}$$

Substituting $\frac{M_1}{M_2} = \frac{5}{4}$ and $\frac{V_1}{V_2} = \frac{x}{y}$ we can calculate *x* : *y*.]

5. You are given 500 mL of 2 *N* HCl and 500 mL of 5 *N* HCl. What will be the maximum volume of 3 *M* HCl that you can make from these two solutions?

(a) 250 mL (b) 750 mL (c) 500 mL (d) 1000 mL

6. The mole fraction of a given sample of I_2 in C_6H_6 is 0.2. The molality of I_2 in C_6H_6 is:

(a) 0.32 (b) 3.2 (c) 0.032 (d) 0.48

[Hint: $m = \frac{x_B \times 1000}{(1 - x_B)m_A}$

$m = \frac{0.2 \times 1000}{0.8 \times 78}$

m = molality

x_B = mole fraction of solute

m_A = molar mass of solvent]

7. A 15-volume sample of an H_2O_2 solution is equivalent to:

(a) 5.30 *N* (b) 1.77 *N* (c) 2.68 *N* (d) 7.50 *N*

[Hint: $V = 5.6\,N$

$15 = 5.6\,N$

$N = 2.68$]

8. If P_A is the vapour pressure of a pure liquid *A* and the mole fraction of *A* in the mixture of two liquids *A* and *B* is *x*, the partial vapour pressure of *A* is:

(a) $(1-x)P_A$ (b) xP_A (c) $\frac{x}{(1-x)}P_A$ (d) $\frac{1-x}{x}P_A$

9. Difference between diffusion and osmosis is:

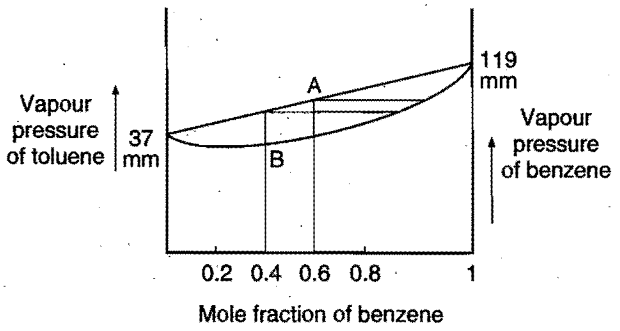
(a) a semipermeable membrane is required for osmosis while diffusion requires no semipermeable membrane

(b) in osmosis, movement of molecules is in one direction whereas in diffusion, the movement is on both sides

(c) in osmosis only the solvent moves while in diffusion solute and solvent both move

(d) all of the above

10.



Choose the correct option:

(a) '*A*' represents vapour composition and '*B*' the liquid composition

(b) '*A*' as well as '*B*' represent liquid composition

(c) Both '*A*' and '*B*' represent vapour composition

(d) '*A*' represents liquid composition and '*B*' the vapour composition

11. Insulin $(C_2H_{10}O_5)_n$ is dissolved in a suitable solvent and the osmotic pressure (π) of solutions of various concentrations (g/cc) C is measured at 20°C. The slope of the plot of π against 'C' is found to be 4.65×10^{-3}. The molecular weight of insulin is:

(a) 4.8×10^5 (b) 9×10^5 (c) 3×10^5 (d) 5.17×10^6

[**Hint:** $\pi V = \frac{w_B}{m_B} \times RT$

$$\pi = \left(\frac{w_B}{V}\right)\frac{RT}{m_B}$$

$$\pi = C \times \frac{RT}{m_B} \times 1000 \qquad \text{...(i)}$$

where C = concentration in g/cc,

$$y = x \times m \qquad \text{...(ii)}$$

Comparing eqs. (i) and (ii),

$$\text{Slope} = \frac{RT}{m_B} \times 1000$$

$$m_B = \frac{RT}{\text{Slope}} \times 1000$$

$$= \frac{0.0821 \times 293 \times 1000}{4.65 \times 10^{-3}}$$

$$= 5.17 \times 10^6]$$

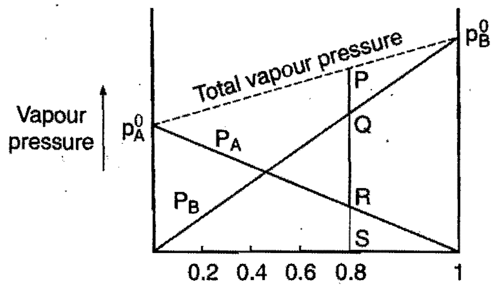
12. Solubility of deliquescent substances in water is generally:

(a) high (b) low

(c) moderate (d) cannot be predicted

[**Hint:** A deliquescent substance absorbs large amount of water, hence solubility is very high.]

13. Consider the following vapour pressure-composition graph, SP is equal to:



(a) $PQ + RS$ (b) $PQ + QR + RS$

(c) $SR + SQ$ (d) $PQ + QR$

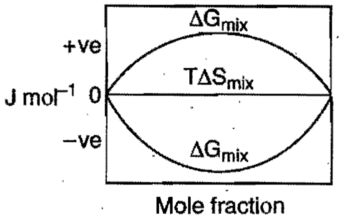
14. y g of a non-volatile organic substance of molecular mass M is dissolved in 250 g benzene. Molal elevation constant of benzene is K_b. Elevation in its boiling point is given by:

(a) $\frac{M}{K_b y}$ (b) $\frac{4K_b y}{M}$ (c) $\frac{K_b y}{4M}$ (d) $\frac{K_b y}{M}$

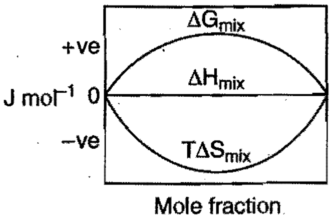
[**Hint:** $\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$

$$= K_b \times \frac{y \times 1000}{M \times 250} = \frac{4K_b y}{M}]$$

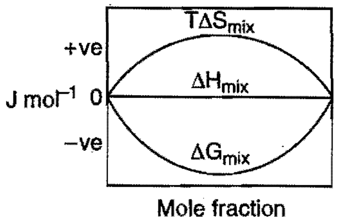
15. Which of the following represents correctly the changes in thermodynamic properties during the formation of 1 mole of an ideal binary solution?



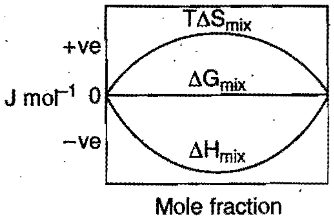
(a)



(b)



(c)



(d)

16. A solute forms a pentamer when dissolved in a solvent. The van't Hoff factor 'i' for the solute will be:

(a) 0.2 (b) 0.8 (c) 0.5 (d) 0.6

17. What is the molarity of HCl in a solution prepared by dissolving 5.5 g HCl in 200 g ethanol if the density of the solution is 0.79 g mL^{-1}?

(a) 21 M (b) 0.93 M (c) 6×10^{-4} M (d) 1.7 M

(e) 0.58 M

[**Hint:** $V = \frac{W\text{ (mass)}}{d} = \frac{205.5}{0.79} = 260.13$ mL

$$M = \frac{w_B \times 1000}{m_B \times V}$$

$$= \frac{5.5 \times 1000}{36.5 \times 260.13} = 0.58\ M]$$

18. Which statement about the composition of vapour over an ideal 1:1 molar mixture of benzene and toluene is correct? Assume the temperature is constant at 25°C.

Vapour pressure data (25°C):

Benzene	75 mm Hg
Toluene	22 mm Hg

(a) The vapour will contain higher percentage of benzene

(b) The vapour will contain higher percentage of toluene

(c) The vapour will contain equal amount of benzene and toluene

(d) Not enough information is given to make a prediction

[**Hint:** A : Benzene B : Toluene

$$p = p_A + p_B$$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 75 \times \frac{1}{2} + 22 \times \frac{1}{2}$$

$$= 37.5 + 11 = 48.5$$

Mole fraction of benzene in vapour, $y_A = \frac{p_A}{p} = \frac{37.5}{48} = 0.78$

Similarly, mole fraction of toluene in vapour, $y_B = 0.22$

∴ The vapour will contain higher percentage of benzene.]

19. When 1.2 g of sulphur is melted with 15 g of naphthalene, the solution freezes at 77.2°C. What is the molar mass of this form of sulphur?

Data for naphthalene:

Melting point (m.pt.) 80°C

Freezing point depression constant K_f 6.80 K m^{-1}

(a) 180 g mol^{-1} (b) 190 g mol^{-1}
(c) 260 g mol^{-1} (d) 450 g mol^{-1}

[**Hint:** $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$$m_B = \frac{K_f}{\Delta T} \times \frac{w_B \times 1000}{w_A}$$

$$= \frac{6.8}{2.8} \times \frac{1.2 \times 1000}{15} \approx 190]$$

20. Which concentrations can be calculated if the mole fraction and density of an aqueous solution of HCl are known?

1. Molality 2. Molarity 3. Percentage by mass

(a) 1 only (b) 3 only
(c) 1 and 2 only (d) 1, 2 and 3

21. The vapour pressure of a liquid in a closed container depends on:

(1) temperature of liquid (2) quantity of liquid
(3) surface area of the liquid

(a) 1 only (b) 2 only
(c) 1 and 3 only (d) 1, 2 and 3

22. A solution is prepared by dissolving a 2.5 g sample of an unknown compound in 34 g of benzene (C_6H_6) boils at 1.38°C higher than pure benzene. Which expression gives the molar mass of the unknown compound?

Compound	K_b
C_6H_6	2.53°C m^{-1}

(a) $2.53 \times \frac{2.50}{1.38}$ (b) $1.38 \times \frac{34}{2.53} \times 2.50$

(c) $2.5 \times 10^3 \times \frac{2.53}{34} \times \frac{1}{1.38}$ (d) $2.50 \times 10^3 \times \frac{1.38}{34} \times 2.53$

23. If liquids A and B form an ideal solution:

(a) the free energy of mixing is zero
(b) the free energy as well as entropy of mixing are zero
(c) enthalpy of mixing is zero
(d) the entropy of mixing is zero

24. Solute A is a ternary electrolyte and solute B is a non-electrolyte. If 0.1 M solution of B produces an osmotic pressure of $2P$ at temperature $3T$ K then 0.05 M solution of A at T K will produce an osmotic pressure of:

(a) P (b) $1.5P$ (c) $2P$ (d) $10P$

25. Which of the following plots represents the behaviour of an ideal binary liquid solution?

(a) Plot of P_{total} *vs* y_A (mole fraction of A in vapour) is linear
(b) Plot of P_{total} *vs* y_B is linear
(c) Plot of $1/P_{\text{total}}$ *vs* y_A is linear
(d) Plot of $1/P_{\text{total}}$ *vs* y_B is non-linear

26. Total vapour pressure of mixture of 1 mol A ($p_A^0 = 150$ torr) and 2 mol B ($p_B^0 = 240$ torr) is 200 torr. In this case:

(a) there is positive deviation from Raoult's law
(b) there is negative deviation from Raoult's law
(c) there is no deviation from Raoult's law
(d) molecular masses of A and B are also required for calculating the deviation

[**Hint:** $x_A = \frac{1}{3}, x_B = \frac{2}{3}$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 150 \times \frac{1}{3} + 240 \times \frac{2}{3} = 50 + 160 = 210 \text{ mm}$$

$$p_{\text{exp.}} < p_{\text{calculated}}$$

∴ There is negative deviation from Raoult's law.]

27. A compound MX_2 has observed and normal molar masses 65.6 and 164 respectively. Calculate the apparent degree of ionization of MX_2:

(a) 75% (b) 85% (c) 65% (d) 25%

[**Hint:** $i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$

$$= \frac{164}{65.6} = 2.5$$

$$\alpha = \frac{i-1}{n-1}, \quad n = 3 \text{ (number of ions)}$$

$$= \frac{2.5-1}{3-1} = \frac{1.5}{2} = 0.75$$

∴ Percentage ionization of MX_2 will be 75%.]

28. Compound $PdCl_4 \cdot 6H_2O$ is a hydrated complex; 1 molal aqueous solution of it has freezing point 269.28 K. Assuming 100% ionization of complex, calculate the molecular formula of the complex (K_f for water = 1.86 K kg mol^{-1}):

(a) $[Pd(H_2O)_6]Cl_4$ (b) $[Pd(H_2O)_4Cl_2]Cl_2 \cdot 2H_2O$
(c) $[Pd(H_2O)_3Cl_3]Cl \cdot 3H_2O$ (d) $[Pd(H_2O)_2Cl_4] \cdot 4H_2O$

[**Hint:** $\Delta T = i \times K_f \times m$

$$(273 - 269.28) = i \times 1.86 \times 1$$

$$3.72 = i \times 1.86$$

$$i = 2$$

$$\alpha = \frac{i-1}{n-1}$$

$$1 = \frac{2-1}{n-1} \text{ or } n = 2$$

Thus, the complex should give two ions in the solution, *i.e.*, the complex will be $[Pd(H_2O)_3Cl_3]Cl \cdot 3H_2O]$

29. Inulin is dissolved in suitable solvent and the osmotic pressure (π) of solutions of various concentrations (g/cm^3) C is measured at 27°C. The slope of plot of π against C is found to be 4.1×10^{-3}. The molecular mass of inulin is:

(a) 6×10^6 (b) 3×10^6 (c) 6×10^3 (d) 3×10^3

[**Hint:** $\pi V = nRT$

$$\pi V = \frac{w}{m} RT$$

$$\pi = \left(\frac{w}{V}\right) \times \frac{1}{m} RT$$

$$\pi = C\left(\frac{RT}{m}\right) \quad \text{... (i)}$$

$$y = MX \quad \text{... (ii)}$$

Slope of the line will be $\frac{RT}{m}$,

i.e., $\frac{RT}{m} = 4.1 \times 10^{-3}$

$$m = \frac{RT}{4.1 \times 10^{-3}} = \frac{0.0821 \times 1000 \times 300}{4.1 \times 10^{-3}}$$

$$= 6 \times 10^6]$$

30. pH of a 0.1 *M* monobasic acid is measured to be 2. Its osmotic pressure at a given temperature *T* K is:

(a) $0.1RT$ (b) $0.11RT$ (c) $1.1RT$ (d) $0.01RT$

[Hint: $HA \rightleftharpoons H^+ + A^-$

$$\begin{array}{llll} t=0 & C & 0 & 0 \\ t_{eq.} & C - C\alpha & C\alpha & C\alpha \end{array}$$

$$[H^+] = C\alpha; [H^+] = 10^{-pH}$$

$$\therefore \quad C\alpha = 10^{-2}$$

$$0.1\alpha = 10^{-2}$$

$$\alpha = 0.1$$

$$\alpha = \frac{i-1}{n-1}; 0.1 = \frac{i-1}{2-1}$$

$$i = 1.1$$

$$\therefore \quad \pi = iCRT$$

$$= 1.1 \times 0.1 \times RT = 0.11RT]$$

31. The amount of ice that will separate on cooling a solution containing 50 g of ethylene glycol in 200 g water at –9.3°C, $K_f = 1.86 \text{ K kg mol}^{-1}$:

(a) 38.71 g (b) 38.71 mg (c) 42 g (d) 42 mg

[Hint: $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$$9.3 = 1.86 \times \frac{50 \times 1000}{62 \times w_A}$$

$w_A = 161.29$ g (amount of water present at – 9.3°C)

$\therefore$ Amount of ice separated = 200 – 161.29

= 38.71 g]

32. 2 moles each of liquids *A* and *B* are dissolved to form an ideal solution. What will be the mole fraction of *B* in the vapour phase?

$p_A^0 = 120$ torr; $p_B^0 = 80$ torr.

(a) 1/4 (b) 1/2 (c) 3/5 (d) 2/5

[Hint: $p = p_A + p_B$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 120 \times \frac{2}{4} + 80 \times \frac{2}{4}$$

$$= 60 + 40 = 100 \text{ torr}$$

y_B = mole fraction of *B* in the vapour phase

$$= \frac{p_B}{p_{\text{total}}} = \frac{40}{100} = \frac{2}{5}]$$

33. Lowering of vapour pressure in 1 molal aqueous solution at 100°C is:

(a) 13.44 mm Hg (b) 14.12 mm Hg

(c) 31.2 mm Hg (d) 35.2 mm Hg

[Hint: Molality and mole fraction are related as follows:

$$m = \frac{x_B \times 1000}{(1 - x_B)m_A}$$

$m = 1$

x_B = mole fraction of solute

m_A = molar mass of solvent

$$1 = \frac{x_B \times 1000}{(1 - x_B) \times 18}$$

$$x_B = 0.0176, \quad x_A = 0.9824$$

$$p = p_0 x_A$$

$$p = 760 \times 0.9824$$

$$= 746.624$$

$$\Delta p = p_0 - p = 760 - 746.624$$

$$\approx 13.4 \text{ mm Hg}]$$

34. The temperature at which the molarity of pure water is equal to its molality is:

(a) 273 K (b) 298 K

(c) 277 K (d) none of these

35. Isopiestic solutions have:

(a) same vapour pressure (b) same osmotic pressure

(c) same freezing point (d) same boiling point

36. Molarity and molality of a solution of caustic soda are respectively 11.12 *M* and 94.12 *m*. The density of the solution is:

(a) 0.556 g mL^{-1} (b) 5.56 g mL^{-1}

(c) 55.6 g mL^{-1} (d) none of these

[Hint: $d = M\left(\frac{1}{m} + \frac{\text{molar mass of solute}}{1000}\right)$

$$d = 11.12\left(\frac{1}{94.12} + \frac{40}{1000}\right)$$

$$= 0.556 \text{ g mL}^{-1}]$$

37. Which of the following solutions has osmotic pressure nearer to that of equimolar solution of $K_4[Fe(CN)_6]$?

(a) Na_2SO_4 (b) $BaCl_2$

(c) $Al_2(SO_4)_3$ (d) $C_{12}H_{22}O_{11}$

38. Equal amounts of a solute are dissolved in equal amounts of two solvents *A* and *B*. The lowering of vapour pressure for the solution *A* is twice the lowering of vapour pressure for the solution *B*. If M_A and M_B are the molecular weights of solvents *A* and *B* respectively, then:

(a) $M_A = M_B$ (b) $M_A = M_B / 2$

(c) $M_A = 4M_B$ (d) $M_A = 2M_B$

Following questions may have more than one correct options:

1. Consider the following solutions:

I. 1 *M* sucrose II. 1 *M* KCl

III. 1 *M* benzoic acid in benzene IV. 1 *M* $(NH_3)_3PO_4$

Which of the following is/are true?

(a) All solutions are isotonic

(b) III is hypotonic of I, II and IV

(c) I, II and III are hypertonic of IV

(d) IV is hypertonic of I, II and III

2. Osmotic pressure of the solution depends on:

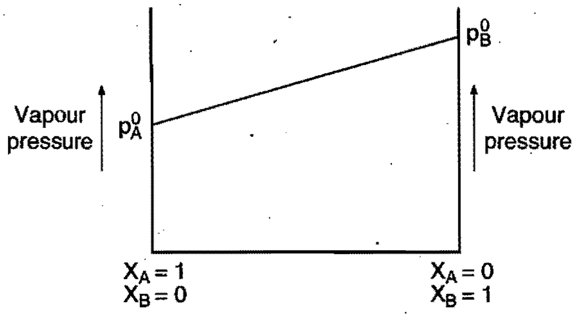
(a) nature of solute

(b) nature of solvent

(c) temperature

(d) molar concentration of solute

3. The following is a graph plotted between the vapour pressures of two volatile liquids against their respective mole fractions.



Which of the following statements are correct?

(a) When $x_A = 1$ and $x_B = 0$, then $p = p_A^0$

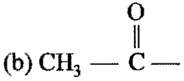
(b) When $x_B = 1$ and $x_A = 0$, then $p = p_B^0$

(c) When $x_A = 1$ and $x_B = 0$, then $p < p_B^0$

(d) When $x_B = 1$ and $x_A = 0$, then $p > p_A^0$

4. Which of the following combinations are correct for a binary solution, in which the solute as well as solvent are liquid?

(a) C_6H_6 and $C_6H_5CH_3$; $\Delta H_{Sol} > 0$; $\Delta V_{Sol} = 0$



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(b) $CH_3-C(=O)-CH_3$ and $CHCl_3$; $\Delta H_{Sol} < 0$; $\Delta V_{Sol} < 0$

(c) H_2O and HCl; $\Delta H_{Sol} > 0$; $\Delta V_{Sol} < 0$

(d) H_2O and C_2H_5OH; $\Delta H_{Sol} > 0$; $\Delta V_{Sol} > 0$

5. A solution containing 0.1 g of a non-volatile organic substance P (molecular mass 100) in 100 g of benzene raises the boiling point of benzene by 0.2° C, while a solution containing 0.1 g of another non-volatile substance Q in the same amount of benzene raises the boiling point of benzene by 0.4° C. What is the ratio of molecular masses of P and Q? **(SCRA 2007)**

(a) 1 : 2 (b) 2 : 1 (c) 1 : 4 (d) 4 : 1

[Hint :

$$\frac{(\Delta T)_P}{(\Delta T)_Q} = \frac{K_b \times \left(\frac{w_B \times 1000}{m_B \times w_A}\right)_P}{K_b \times \left(\frac{w_B \times 1000}{m_B \times w_A}\right)_Q}$$

$$\frac{0.2}{0.4} = \frac{\left(\frac{0.1 \times 1000}{100 \times 100}\right)_P}{\left(\frac{0.1 \times 1000}{100 \times m_B}\right)_Q}$$

$$\frac{1}{2} = \frac{(m_B)_Q}{100}$$

$$m_B = 50$$

$$\therefore \ (m_B)_P : (m_B)_Q = 100 : 50$$

$$= 2 : 1]$$

6. Consider 0.1 M solution of two solutes X and Y. The solute X behaves as uni-univalent electrolyte while the solute Y dimerises in solution. Which of the following statements are correct regarding these solutions?

1. The boiling point of solution of X will be higher than that of Y
2. The osmotic pressure of solution of Y will be lower than that of X
3. The freezing point of the solution of X will be lower than that of Y
4. The relative lowering of vapour pressure of both the solutions will be the same

Select the correct answer from the codes given below:

(a) 1, 2, 3 (b) 2, 3, 4 (c) 1, 2, 4 (d) 1, 3, 4

7. For a given value of degree of dissociation, which of the following have correct van't Hoff factor?

(a) NaCl $i = 2 + \alpha$

(b) $Ca(NO_3)_2$ $i = 1 + 2\alpha$

(c) $K_4[Fe(CN)_6]$ $i = 1 + 4\alpha$

(d) $(NH_3)_3PO_4$ $i = 3 + \alpha$

8. 1 mole benzene ($p^0_{benzene} = 42$ mm) and 2 mole toluene ($p^0_{toluene} = 36$ mm) will have:

(a) total vapour pressure 38 mm

(b) mole fraction of vapours of benzene above liquid mixture is 7/19

(c) positive deviation from Raoult's law

(d) negative deviation from Raoult's law

[Hint: $p = p_A^0 x_A + p_B^0 x_B$ $A \rightarrow$ Benzene, $B \rightarrow$ Toluene

$$= 42 \times \frac{1}{3} + 36 \times \frac{2}{3}$$

$$= \frac{114}{3} = 38 \text{ mm}$$

$$\text{Mole fraction of benzene in vapour} = \frac{p_{benzene}}{p_{total}} = \frac{42/3}{38}$$

$$= 7/19]$$

9. The decrease in freezing point of an aqueous solution of a substance is 1.395 K and that in the freezing point of a benzene solution of the same substance is 1.28 K. The substance:

(a) dissociates in aqueous solution as well as in the benzene solution

(b) forms complexes in the solution

(c) associates in the benzene solution

(d) dissociates in the aqueous solution and not in the benzene solution

10. The vapour pressure of water at T (K) is 20 mm Hg. The following solutions are prepared at T (K):

I. 6 g of urea (mol. wt. = 60) is dissolved in 178.2 g of water.
II. 0.01 mole of glucose is dissolved in 179.82 g of water.
III. 5.3 g of Na_2CO_3 (mol. wt. = 106) is dissolved in 179.1 g of water.

Identify the correct order in which the vapour pressures of solutions increase: **[EAMCET (Medical) 2006]**

(a) III, I, II (b) II, III, I (c) I, II, III (d) I, III, II

[Hint:

I. $$x_B = \frac{n_B}{n_A + n_B} = \frac{6/60}{178.2/18} + \frac{6}{60}$$

$$= 0.01$$

$$\frac{\Delta p}{p_0} = x_B = 0.01$$

II. $$x_B = \frac{n_B}{n_A + n_B} = \frac{0.01}{\frac{179.82}{18} + 0.01}$$

$$= 0.001$$

$$\frac{\Delta p}{p_0} = 0.001$$

III. $$x_B = \frac{n_B}{n_A + n_B} = \frac{5.3/106}{\frac{179.1}{18} + \frac{5.3}{106}} = 0.005$$

$$\frac{\Delta p}{p_0} = ix_B$$

$$= 3 \times 0.005$$

$$= 0.015$$

∴ Vapour pressures of solutions will increase in the following sequence:

(III) < (I) < (II).]

11. Consider lowering of vapour pressure (Δp), elevation in boiling point (ΔT_b) and depression in freezing point (ΔT_f) of a solvent for the same molar concentration of each of the following three solutes :

1. $BaCl_2$ 2. NaCl 3. $MgCl_2$

Which of the following is/are the correct sequence?

(SCRA 2009)

(a) $\Delta p : 3 < 2 < 1$ (b) $\Delta T_b : 1 > 2 > 3$

(c) $\Delta T_f : 3 < 2 < 1$ (d) None of these

[**Hint :** van't Hoff factor of both $BaCl_2$ and $MgCl_2$ are same, *i.e.*, 3, hence none of the given sequence are correct.]

Answers

• Single correct option

1. (b) **2.** (d) **3.** (a) **4.** (a) **5.** (b) **6.** (b) **7.** (c) **8.** (b)
9. (d) **10.** (c) **11.** (d) **12.** (a) **13.** (c) **14.** (b) **15.** (c) **16.** (a)
17. (e) **18.** (b) **19.** (b) **20.** (d) **21.** (a) **22.** (c) **23.** (c) **24.** (a)
25. (c) **26.** (b) **27.** (a) **28.** (c) **29.** (a) **30.** (b) **31.** (a) **32.** (d)
33. (a) **34.** (c) **35.** (a) **36.** (a) **37.** (c) **38.** (b)

• One or more than one correct options

1. (b, c, d) **2.** (c, d) **3.** (a, b) **4.** (b, d) **5.** (b) **6.** (a) **7.** (b, c) **8.** (a, b)
9. (c, d) **10.** (a) **11.** (d)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

A 1.24 M aqueous solution of KI has density of $1.15\ g/cm^3$.

Answer the following questions about this solution:

1. Percentage composition of solute in the solution is:
   (a) 17.89 (b) 27.89 (c) 37.89 (d) 47.89
2. Molality of this solution will be:
   (a) 2.61 (b) 1.31 (c) 4.12 (d) 3.12
3. What is the freezing point of the solution if the KI is completely dissociated in the solution?
   (a) – 4.87°C (b) – 3.22°C
   (c) – 1.22°C (d) None of these
4. Experimental freezing point of the solution is – 4.46°C. What % of KI is dissociated?
   (a) 82% (b) 90% (c) 83% (d) None
5. Normality of this solution is:
   (a) 0.62 (b) 1.24 (c) 2.48 (d) 3.72

• Passage 2

The colligative properties of electrolytes require a slightly different approach than the one used for the colligative properties of non-electrolytes. The electrolytes dissociate into ions in a solution. It is the number of solute particles that determines the colligative properties of a solution. The electrolyte solutions, therefore, show abnormal colligative properties. To account for this effect we define a quantity called the van't Hoff factor, given by:

$$i = \frac{\text{Actual number of particles in solution after dissociation}}{\text{Number of formula units initially dissolved in solution}}$$

$i = 1$ (*for non-electrolytes*);

$i > 1$ (*for electrolytes, undergoing dissociation*)

$i < 1$ (*for solutes, undergoing association*).

Answer the following questions:

1. Benzoic acid undergoes dimerisation in benzene solution. The van't Hoff factor 'i' is related to the degree of association 'α' of the acid as:
   (a) $i = 1 - \alpha$ (b) $i = 1 + \alpha$
   (c) $i = 1 - \frac{\alpha}{2}$ (d) $i = 1 + \frac{\alpha}{2}$
2. A substance trimerises when dissolved in a solvent A. The van't Hoff factor 'i' for the solution is:
   (a) 1 (b) 1/3
   (c) 3 (d) unpredictable
3. For a solution of a non-electrolyte in water, the van't Hoff factor is:
   (a) always equal to 0 (b) ≤ 1
   (c) always equal to 2 (d) > 1 but < 2
4. 0.1 M $K_4[Fe(CN)_6]$ is 60% ionized. What will be its van't Hoff factor?
   (a) 1.4 (b) 2.4 (c) 3.4 (d) 4.4

   [**Hint:** $\alpha = \frac{i-1}{n-1}$, $n = 5$ since, $K_4[Fe(CN)_6]$ gives 5 ions in the solution

   $0.6 = \frac{i-1}{5-1}$

   $i = 3.4$]
5. A solution of benzoic acid dissolved in benzene such that it undergoes molecular association and its molar mass approaches 244. Benzoic acid molecules will exist as:
   (a) dimer (b) monomer
   (c) tetramer (d) trimer
6. The molar mass of the solute sodium hydroxide obtained from the measurement of the osmotic pressure of its aqueous solution at 27°C is 25 g mol^{-1}. Therefore, its dissociation percentage in this solution is: **[CET (J&K) 2009]**
   (a) 75 (b) 60
   (c) 80 (d) 70

   [**Hint:** $i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$ ...(i)

   $\alpha = \frac{i-1}{n-1}$

   $i = 1 + \alpha$ for binary electrolyte

   $\therefore\quad 1 + \alpha = \frac{40}{25};\ \alpha = 0.6$

   % ionisation = 60]

• Passage 3

Many chemical and biological processes depend on osmosis which is, the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one. The osmotic pressure π depends on molar concentration of the solution ($\pi = CRT$). *If two solutions are of equal solute concentration and, hence, have the same osmotic pressure, they are said to be* ***isotonic.*** *If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be* ***hypertonic*** *and the more diluted solution is described as* ***hypotonic.***

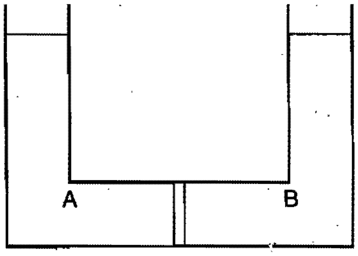
Osmosis is the major mechanism for transporting water upward in the plants. Transpiration in the leaves supports the transport mechanism of water. The osmotic pressure of seawater is about 30 atm; this is the pressure that must be applied to the seawater (separated from pure water using a semipermeable membrane) to get drinking water.

Answer the following questions:

1. A plant cell shrinks when it is kept in:
   (a) hypotonic solution (b) hypertonic solution
   (c) isotonic solution (d) pure water
2. 4.5% solution of glucose would be isotonic with respect to .... solution of urea.
   (a) 4.5% (b) 13.5%
   (c) 1.5% (d) 9%
3. Glucose solution to be injected into the bloodstream must have same ..... as that of the bloodstream.
   (a) molarity (b) vapour pressure
   (c) osmotic pressure (d) viscosity

4. Isotonic solutions have same:
   (a) density (b) molarity
   (c) molality (d) mole fraction
   (e) normality
5. Osmotic rise of a solution depends on:
   (a) density (b) temperature
   (c) nature of solvent (d) none of these

• Passage 4



Compartments 'A' and 'B' have the following combinations of solutions:

	A	*B*
1.	*0.1 M KCl*	*0.2 M KCl*
2.	*0.1% (m/V) NaCl*	*10% (m/V) NaCl*
3.	*18 g/L glucose*	*34.2 g/L sucrose*
4.	*20% (m/V) glucose*	*10% (m/V) glucose*

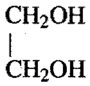
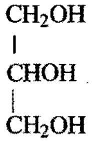
Answer the following questions:

1. Indicate the solutions which is/are isotonic:
   (a) 1 only (b) 3 only (c) 4 only (d) 2 only
2. The solutions in which the compartment '*B*' is hypertonic:
   (a) 1, 2 (b) 2, 3 (c) 3, 4 (d) 1, 4
3. Indicate the solution(s) in which the compartment '*A*' will show the increase in volume:
   (a) 1 (b) 2 (c) 3 (d) 4
4. Indicate the solution(s) in which the compartment '*B*' will show the increase in volume:
   (a) 1, 2, 4 (b) 1, 2 (c) 2, 3 (d) 3, 4
5. The solution in which there will be no change in the level of the solution in the compartments '*A*' and '*B*' is:
   (a) 1 (b) 2 (c) 3 (d) 4

• Passage 5

The boiling point elevation and the freezing point depression of solutions have a number of practical applications. Ethylene glycol ($CH_2OH \cdot CH_2OH$) *is used in automobile radiators as an antifreeze because it lowers the freezing point of the coolant. The same substance also helps to prevent the radiator coolant from boiling away by elevating the boiling point. Ethylene glycol has low vapour pressure. We can also use glycerol as antifreeze. For boiling point elevation to occur, the solute must be non-volatile, but no such restriction applies to freezing point depression. For example, methanol* (CH_3OH)*, a fairly volatile liquid that boils only at 65°C is sometimes used as antifreeze in automobile radiators.*

Answer the following questions:

1. Which of the following is a better reagent for depression in freezing point but not for elevation in boiling point?
   (a) CH_3OH (b) 
   $\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$
   (c) 
   $\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$
   (d) $C_6H_{12}O_6$
2. 124 g each of the two reagents glycol and glycerol are added in 5 kg water of the radiators in the two cars. Which of the following statements is wrong?
   (a) Both will act as antifreeze
   (b) Glycol will be better
   (c) Glycerol is better because its molar mass is greater than glycol
   (d) Glycol is more volatile than glycerol
3. 620 g glycol is added to 4 kg water in the radiator of a car. What amount of ice will separate out at – 6°C? $K_f = 1.86$ K kg mol^{-1}:
   (a) 800 g (b) 900 g (c) 600 g (d) 1000 g
4. If cost of glycerol, glycol and methanol are same, then the sequence of economy to use these compounds as antifreeze will be:
   (a) glycerol > glycol > methanol
   (b) methanol > glycol > glycerol
   (c) methanol = glycol = glycerol
   (d) methanol > glycol < glycerol
5. Which among the following is the most volatile and the best antifreeze?
   (a) CH_3OH (b) C_2H_5OH (c) Glycol (d) Glycerol

• Passage 6

The solutions which boil at constant temperature like a pure liquid and possess same composition in liquid as well as vapour state are called azeotropes. The components of azeotropes cannot be separated by fractional distillation. Only non-ideal solutions form azeotropes. Solutions with negative deviation form maximum boiling azeotrope and the solutions with positive deviation form minimum boiling azeotrope. Boiling point of an azeotrope is never equal to the boiling points of any of the components of the azeotrope.

Answer the following questions:

1. The azeotropic solutions of two miscible liquids:
   (a) can be separated by simple distillation
   (b) may show positive or negative deviation from Raoult's law
   (c) are supersaturated
   (d) behave like single pure component and boil at a fixed temperature
2. Solutions which distill without any change in composition or temperature are called:
   (a) saturated (b) supersaturated
   (c) ideal (d) azeotrope
3. The azeotropic mixture of water and HCl boils at 108.5°C. This solution is:
   (a) ideal
   (b) non-ideal with positive deviation
   (c) non-ideal with negative deviation
   (d) cannot be predicted

4. 100 mL liquid A and 50 mL liquid B are mixed to form 138 mL solution. It is:
   (a) ideal solution (b) high boiling azeotrope
   (c) low boiling azeotrope (d) none of these
5. Which among the following combinations is maximum boiling azeotrope?
   (a) $H_2O + CH_3OH$ (b) $CCl_4 + CHCl_3$
   (c) $(CH_3)_2CO + C_2H_5OH$ (d) $H_2O + HNO_3$

• Passage 7

The properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water.

The mole fraction of ethanol in the mixture is 0.9.

Given : Freezing point depression constant of water (K_f *for water*) $= 1.86\,K\ kg\ mol^{-1}$

Freezing point depression constant of ethanol (K_f *for ethanol*) $= 2.0\,K\ kg\ mol^{-1}$

Boiling point elevation constant of water (K_b *for water*) $= 0.52\,K\ kg\ mol^{-1}$

Boiling point elevation constant of ethanol (K_b *for ethanol*) $= 1.2\,K\ kg\ mol^{-1}$

Standard freezing point of water $= 273\ K$
Standard freezing point of ethanol $= 155.7\ K$
Standard boiling point of water $= 373\ K$
Standard boiling point of ethanol $= 351.5\ K$
Vapour pressure of pure water $= 32.8\ mm\ Hg$
Vapour pressure of pure ethanol $= 40\ mm\ Hg$
Molecular weight of water $= 18\ g\ mol^{-1}$
Molecular weight of ethanol $= 46\ g\ mol^{-1}$

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

Answer the following questions:

1. The freezing point of the solution M is:
   (a) 268.7 K (b) 268.5 K (c) 234.2 K (d) 150.9 K
2. The vapour pressure of the solution M is:
   (a) 39.3 mm Hg (b) 36.0 mm Hg
   (c) 29.5 mm Hg (d) 28.8 mm Hg
3. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is:
   (a) 380.4 K (b) 376.2 K (c) 375.5 K (d) 354.7 K

(IIT 2008)

[**Hint:**

1. Molality $m = \dfrac{x_B \times 1000}{(1 - x_B)\, m_A} = \dfrac{0.1 \times 1000}{0.9 \times 46}$

$$= 2.415$$

$$\Delta T = K_f \times m$$

$$= 2 \times 2.415 = 4.83$$

Freezing point of solution $= 155.7 - 4.83 = 150.9$ K

2. $p = p^0 x_A$

$$= 40 \times 0.9 = 36 \text{ mm Hg}$$

3. When water becomes solvent, the molality of solution will be :

$$m = \frac{x_B \times 100}{x_A \times m_A} = \frac{0.1 \times 1000}{0.9 \times 18} = 6.172$$

$$\Delta T = K_b \times m = 0.52 \times 6.172 = 3.209$$

Boiling point of solution $= 373 + 3.209$

$= 376.2$ K]

Answers

Passage 1.	1. (a)	2. (b)	3. (a)	4. (c)	5. (b)	
Passage 2.	1. (c)	2. (b)	3. (b)	4. (c)	5. (a)	6. (b)
Passage 3.	1. (b)	2. (c)	3. (c)	4. (b)	5. (a, b)	
Passage 4.	1. (b)	2. (a)	3. (d)	4. (b)	5. (c)	
Passage 5.	1. (a)	2. (c)	3. (b)	4. (b)	5. (a)	
Passage 6.	1. (b, d)	2. (d)	3. (c)	4. (b)	5. (d)	
Passage 7.	1. (d)	2. (b)	3. (b)			

SELF ASSESSMENT

ASSIGNMENT NO. 5

SECTION-I

Straight Objective Type Questions

This section contains 12 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. The relative lowering of vapour pressure of a dilute aqueous solution containing non-volatile solute is 0.0125. The molality of solution is about: **[PET (Kerala) 2007]**
(a) 0.70 (b) 0.50 (c) 0.90 (d) 0.80
(e) 0.60

2. If the elevation in boiling point of a solution of 10 gm of solute (mol. mass = 100) in 100 g of water is ΔT_b, the ebullioscopic constant of water is: **[PET (Kerala) 2007]**
(a) 10 (b) $100\,T_b$ (c) ΔT_b (d) $\frac{\Delta T_b}{10}$
(e) $10\,T_b$

3. Which one of the following aqueous solutions will exhibit highest boiling point? **(DPMT 2009)**
(a) 0.1 M KNO_3 (b) 0.1 M Na_3PO_4
(c) 0.1 M $BaCl_2$ (d) 0.1 M K_2SO_4

4. A solution containing 10 g per dm^3 of urea (molecular mass = 60 g mol^{-1}) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of this non-volatile solute is: **(AIIMS 2007)**
(a) 300 g mol^{-1} (b) 350 g mol^{-1}
(c) 200 g mol^{-1} (d) 250 g mol^{-1}

5. The molarity of 5 molal aqueous solution of NaOH having density 1.2 g / cc is:
(a) 5 M (b) 4.1 M (c) 6 M (d) 8 M

6. The value of osmotic pressure does not depend on:
(a) concentration of solution
(b) van't Hoff factor
(c) temperature
(d) structure of solute particles

7. Henry's law constants for O_2 and N_2 are:

$$k_{O_2} = 3.3 \times 10^7, k_{N_2} = 6.51 \times 10^7$$

Calculate the ratio of $\frac{x_{O_2}}{x_{N_2}}$, *i.e.*, the ratio of mole fractions of O_2 and N_2 dissolved in water at 25° C from air:
(a) 0.62 (b) 0.92 (c) 0.42 (d) 0.52

8. The molal lowering of vapour pressure of water at 100° C is:
(a) 13.68 mm (b) 46 mm
(c) 65 mm (d) 13.68 cm

9. USP ethanol in aqueous solution in containing 95% ethanol by volume. At 20° C, pure ethanol has a density of 0.789 g/mL and USP ethanol density 0.813 g/mL. What is the mass percentage of ethanol in USP ethanol?
(a) 46% (b) 90% (c) 86% (d) 92.3%

10. A solution of 7.45 g KCl in 1000 mL shows osmotic pressure of 4.68 atm at 300K. Calculate the percentage dissociation of KCl:
(a) 70% (b) 80% (c) 90% (d) 10%

11. The mass of glucose that should be dissolved in 50g of water in order to produce same lowering of vapour pressure as is produced by dissolving 1 g of urea in the same quantity of water is : **[MGIMS (Wardha) 2008]**
(a) 1 g (b) 3 g (c) 6 g (d) 18 g

12. Consider the following aqueous solutions and assume 100% ionisation in electrolytes :
I. 0.1 m urea II. 0.04 m $Al_2(SO_4)_3$
III 0.05 m $CaCl_2$ IV. 0.005 m NaCl
The correct statement regarding the above solutions is : **[BHU (Mains) 2008]**
(a) freezing point will be lowest for solution I
(b) freezing point will be highest for solution IV
(c) boiling point will be highest for solution IV
(d) Vapour pressure will be highest for solution II

SECTION-II

Multiple Answers Type Objective Questions

13. K_2HgI_4 is 50% ionised in aqueous solution. Which of the following are correct?
(a) $n = 7$ (b) $n = 3$ (c) $i = 2$ (d) $i = 4$

14. Henry's law is invalid for gases like.................
(a) CO_2 (b) SO_2 (c) HCl (d) N_2

15. The azeotropic mixture of two liquids:
(a) boils at constant temperature
(b) can be separated by simple distillation
(c) is super saturated
(d) deviates from Raoult's law

16. Cryoscopic constant of a liquid depends on:
(a) the latent heat of fusion of solvent
(b) the freezing point of solvent
(c) the concentration of solution
(d) the melting point of solute

17. Which of the following is/are influenced by the temperature?
(a) Freezing point (b) Boiling point
(c) Vapour pressure (d) Osmotic pressure

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.

(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

18. **Statement-1:** Solubility of ionic compounds in water depends on both the lattice energy and the hydration energy.

Because

Statement-2: Ionic compounds dissolve in water when their hydration energy exceeds the lattice energy.

19. **Statement-1:** Isotonic solutions have same molar concentration.

Because

Statement-2: Solutions which have same osmotic pressure at same temperature are known as isotonic solutions.

[**Hint:** It is not necessary that solutions at same molar concentration have same osmotic pressure, *eg.*, $\pi(0.1M\ \text{NaCl}) > \pi(0.1\,M\ \text{glucose})$ because NaCl is ionised]

20. **Statement-1:** The vapour pressure of 0.1 M Hg_2Cl_2 is equal to 0.1 M $AlCl_3$ solution.

Because

Statement-2: 0.1 M $AlCl_3$ and 0.1 M Hg_2Cl_2 give different numbers of ions in a solution.

21. **Statement-1:** Elevation in boiling point will be high if the molal elevation constant of solvent is high.

Because

Statement-2: Elevation in boiling point is a colligative property.

22. **Statement-1:** Ethylene glycol is used as antifreeze for the radiator of a car.

Because

Statement-2: Ethylene glycol dissolves in water with the help of hydrogen bond and it lowers the freezing point.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statements given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s), (b-q,r), (c-p,q) and (d-s), then correct bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	●	○	○
d	○	○	○	●

23. Match the Column-I with Column II:

Column-I	Column-II
(a) $CCl_4 + CHCl_3$	(p) Raoult's law
(b) $C_6H_6 + H_2O$	(q) Nearly ideal solution
(c) $p_A \propto x_A$	(r) Negative deviation from Raoult's law
(d) $p_A < p_A^0 x_A$	(s) Positive deviation from Raoult's law

24. Match the Column-I with Column II:

Column-I (Species completely ionised)	Column-II (van't Hoff factor)
(a) Hg_2Cl_2	(p) 5
(b) $K_3[Fe(CN)_6]$	(q) 4
(c) $Ca_3(PO_4)_2$	(r) 1
(d) glucose	(s) 3

25. Match the Column-I with Column II:

Column-I	Column-II
(a) Mole fraction	(p) mol kg^{-1}
(b) Molality	(q) Depends on temperature
(c) Molarity	(r) Unitless
(d) Normality	(s) Independent of temperature

Answers

1. (a)	**2.** (c)	**3.** (b)	**4.** (a)	**5.** (a)	**6.** (d)	**7.** (d)	**8.** (a)
9. (d)	**10.** (c)	**11.** (b)	**12.** (b)	**13.** (b, c)	**14.** (a, b, c)	**15.** (a, d)	**16.** (a, b)
17. (c, d)	**18.** (a)	**19.** (d)	**20.** (d)	**21.** (b)	**22.** (a)	**23.** (a-q) (b-s) (c-p, q) (d-r)	
24. (a-s) (b-q) (c-p) (d-r)		**25.** (a-r,s) (b-p,s) (c-q) (d-q)					