SOLUTIONS

NEET SYLLABUS

Solutions : Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, colligative properties- relative lowering of vapour pressure, Raoult's law, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular mass using colligative properties abnormal molecular mass, Van Hoff factor.

OBJECTIVES

After studying this unit, we will be able to :

- *describe the formation of different types of solutions.*
- *express concentration of solution in different units.*
- *state and explain Henry's law and Raoult's law.*
- *distinguish between ideal and non-ideal solutions.*
- *explain deviations of real solutions from Raoult's law.*
- *describe colligative properties of solutions and correlate with molar masses of solutes.*
- *explain abnormal colligative properties exhibited by some solutes in solutions.*

> ***"Imagination equals nostalgia for the past, the absent;***
> ***it is the liquid soultion in which science develops as snapshot of reality"***
>
> **Cyril Connoly**

SOLUTIONS

3.0 INTRODUCTION

3.1 Definition of Solution :

When two or more chemically non-reacting substances are mixed together forming homogeneous mixture the mixture is called solution.

When the solution is composed of only two chemical substances, it is termed as binary solution, similarly, it is called ternary and quaternary if it is composed by three and four components respectively.

For binary solution : Solution = solute + solvent

- Generally the component present in lesser amount than, other component in solution, is called solute.
- Generally, the component present in greater amount than all other components, is called the solvent.
- Physical state of solvent and solution is same.

Solution	Solute + Solvent	
	(B)	(A)
moles	n	N
mass	$w_{(g)}$	$W_{(g)}$
molar mass	m	M
mole fraction	x_B	x_A

Ex.1 In a syrup (liquid solution) containing 60 g sugar (a solid) and 40 g water (a liquid) same aggregation as solution water is termed as the solvent.

Ex.2 : In a solution of alcohol and water ; having 10 mL alcohol and 20 mL water, water is solvent and alcohol will be solute.

- On the basis of amount of solute, solutions can be classified in two ways.

(a) Dilute Solution

A solution in which relatively a small amount of solute is dissolved in large amount of solvent is called a dilute solution.

(b) Concentrated Solution

A solution in which relatively a large amount of the solute is present is called a concentrated solution.

3.2 CONCENTRATION TERMS

(a) Normality (N)

The *number of equivalents* or *gram equivalents* of solute present in *one litre* of the solution is known as normality (N) of the solution.

$$= \frac{\text{Number of gram equivalents of solute (g)}}{\text{Volume of solution (L)}}$$

$$= \frac{\text{Mass of solute (g)}}{\text{Equivalent mass } \times \text{Volume of solution (L)}}$$

(b) Molarity (M)

The *number of moles* of solute present in *one litre* solution is called its molarity(M).

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{volume of solution (L)}} = \frac{n}{V_{(L)}}$$

(c) Formality (F)

It is the number of *gram formula mass units* present per litre of solution. Formality is generally used for solutions of ionic compounds.

$$\text{Formality} = \frac{\text{Mass of solute (g)}}{\text{Formula mass of solute (g)} \times \text{Volume of solution (L)}}$$

(d) Molality (m)

The *number of moles* of solute present in *1000 gram* of the solvent is called molality of the solution.

$$\text{Molality of a solution} = \frac{\text{Number of moles of solute}}{\text{Amount of solvent (kg)}} = \frac{\text{Number of moles of solute} \times 1000}{\text{Amount of solvent (g)}}$$

(e) Strength of a Solution (S)

The mass of solute in g dissolved in 1L solution is known as its strength in g L^{-1}

$$S = \frac{\text{Mass of solute (g)}}{\text{Volume of solution (L)}}$$

$S(gL^{-1})$ = Molarity of solution × Molar mass of solute

$S(gL^{-1})$ = Normality of solution × Equivalent mass of solute

(f) Concentration in terms of percentage

(i) Percent By Mass (w/W)

Mass of solute (in g) present in 100 g of solution (g) is called mass percent of the solute.

Where 'w' gram of solute is dissolved in W gram of solvent.

$$\text{Mass percent} = \frac{\text{Mass of solute (g)} \times 100}{\text{Mass of solution (g)}} = \frac{w \times 100}{w + W}$$

Mass percent is independent of temperature.

(ii) Percent By Volume (v/V)

This method is used for solutions of liquid in a liquid. The volume of liquid (solute) in mL present in 100 mL of solution in is called volume percent.

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

(iii) Percent by strength /percentage mass by volume $\left(\frac{w}{V}\right)$: Mass of solute (in g) present in 100 mL solution is called mass by volume.

$$\%\left(\frac{w}{V}\right) = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100$$

(g) Parts Per Million (ppm)

This method is used for expressing the concentration of very dilute solutions such as hardness of water, air pollution etc.

$$\text{ppm of substance (by mass)} = \frac{\text{Mass of solute (g)} \times 10^6}{\text{Mass of solution (g)}}$$

$$\text{ppm (by volume)} = \frac{\text{Volume of solute(mL)} \times 10^6}{\text{Volume of solution(mL)}}$$

$$\text{ppm}\left(\text{by}\frac{w}{V}\right) = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 10^6$$

(h) Mole Fraction

The ratio of the number of moles of one component to the total number of moles of all the components present in the solution, is called the mole fraction of that component.

Mole fraction of solute $X_B = \dfrac{\text{moles of solute}(n)}{\text{moles of solute }(n)+\text{moles of solvent}(N)}$

Mole fraction of solvent $X_A = \dfrac{\text{moles of solvent}(N)}{\text{moles of solute }(n)+\text{moles of solvent}(N)}$

$$\boxed{X_A + X_B = 1}$$

(i) (i) **Relation Between Molarity and Normality**

S = Molarity × Molar mass of solute and S = Normality × Equivalent mass of solute.

So we can write

Molarity × Molar mass of solute = Normality × Equivalent mass of solute.

$$\text{Normality} = \frac{\text{Molarity} \times \text{Molar mass of solute}}{\text{Equivalent mass of solute}}$$

$$= \frac{\text{Molarity} \times \text{Molar mass of solute}}{(\text{Molar mass of solute/valency factor})}$$

Normality = Molarity × Valency factor

N = M × n factor

(ii) Relation Between Molality (m) and Mole fraction

$$\frac{x_B}{x_A} = \frac{n_B}{N_A} = \frac{n_B \times M_A \times 1000}{w_A \times 1000}$$

$$\frac{x_B}{x_A} = \frac{\text{molality} \times M_A}{1000}$$

$$\frac{x_B}{1-x_B} = \frac{\text{molality } \times M_A}{1000} \text{ : if } x_B <<< 1 \text{ for very dilute } x_B = \frac{\text{molality} \times M_A}{1000}$$

(j) VOLUME STRENGTH OF H_2O_2 SOLUTION :

Volume of O_2 (L) produced by decomposition of unit volume solution of H_2O_2 at NTP/STP; is called its volume strength.

Relationship between volume strength of H_2O_2 and Molarity / Normality / (g/L) / % (w/V)

Let volume strength of H_2O_2 solution be 'X V', it means 1L solution of H_2O_2, can produce X L of O_2 at NTP.

$$2H_2O_2 \longrightarrow 2H_2O + O_2(g)$$
2mol 1mol

∵ 1 mol O_2 can be produced by = 2 mol H_2O_2 solution

$$\therefore \frac{X}{22.4} \text{ mol of } O_2 \text{ can be produced by } = \frac{2X}{22.4} \text{ mol } H_2O_2 \text{ solution}$$

$$= \frac{X}{11.2} \text{ mol of } H_2O_2 \text{ solution}$$

(a) $$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution(L)}} = \frac{2X}{22.4} = \frac{X}{11.2}$$

Hence $\boxed{M = \frac{X}{11.2}}$

(b) $$\text{Normality} = \text{molarity} \times \text{valence factor} = \frac{X}{11.2} \times 2 = \frac{X}{5.6}$$

Hence $\boxed{N = \frac{X}{5.6}}$

(c) Strength (g/L) : $S = N \times E$

Hence $\boxed{S = \frac{X}{5.6} \times 17}$ gL^{-1}

(d) $$\boxed{\%\left(\frac{w}{V}\right) = \frac{X}{5.6} \times \frac{17}{10}}$$

GOLDEN KEY POINTS

- If the density of solution is approximately 1g/cc then Molality > Molarity
- ppm unit is used to represent concentration of very dilute solutions like pollutants in environment and salts present in sea water.
- Those concentration terms which involves volume of solution are temperature dependent.
- Molarity, normality, formality, % by volume, % w/V, are temperature dependent.
- Molality, % w/W, mole fraction are temperature independent.

Illustrations

Illustration 1. If 0.4 g of NaOH is present in 40 mL of solution. What is the molarity and normality of solution [Molecular mass of NaOH = 40]

Solution. We know that

$$\text{Molarity} = \frac{\text{Mass of solute} \times 1000}{\text{Molar Mass of solute} \times \text{Volume of solution (mL)}}$$

$$M = \frac{0.4}{40 \times 40} \times 1000 = 0.25\text{ M}$$

$$\text{Normality} = \frac{\text{Mass of solute}}{\text{Equivalent mass of solute} \times \text{volume of solution(mL)}} \times 1000$$

Equivalent mass of NaOH = 40

$$N = \frac{0.4}{40 \times 40} \times 1000 = 0.25\text{N}$$

Illustraion 2. The normality of 1.5M H_3PO_4 is –

Solution. Basicity of H_3PO_4 is 3

We know that $N = M \times n \Rightarrow$ Normality $= 1.5 \times 3 = 4.5$ N

Illustraion 3. Find out the mass of H_2SO_4 in 150 mL, $\frac{N}{7}$ H_2SO_4.

Solution. $N = \frac{\text{Mass in gram}}{\text{Equivalent mass} \times \text{Volume(L)}}$

Mass in gram = Equivalent mass × N ×Volume (L) = $49 \times \frac{1}{7} \times \frac{150}{1000} = \frac{21}{20} = 1.05\text{g}$

Illustraion 4. Find out the molarity of 93% (w/W) H_2SO_4 (density = 1.84 g/ml).

Solution. $\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution(L)}} = \frac{\text{Mass in gram} \times \text{Density} \times 1000}{\text{Molar mass} \times \text{mass of solution (g)}}$

$= \frac{93 \times 1.84 \times 1000}{98 \times 100} = 17.46\text{ M}$

Illustraion 5. A 100 cm^3 solution is prepared by dissolving 2g of NaOH in water. Calculate the normality of the solution.

Solution. $2\text{g NaOH} = \frac{2}{40}$ g eq; $N = \frac{\frac{1}{20}}{100} \times 1000 = \frac{1}{2}$

Normality of solution = $\frac{N}{2}$

Illustraion 6. Find the percentage by mass and mass fraction of aspirin in the solution prepared by dissolving 3.65 g of aspirin in 25.08 g of water .

Solution. Mass of solution = 3.65 + 25.08 = 28.73 g

Mass fraction $= \frac{3.65}{28.73} = 0.127$

Mass percent = $0.127 \times 100 = 12.7\%$

Illustraion 7. A solution was prepared by adding 125 cm^3 of isopropyl alcohol to water until the volume of the solution was 175 cm^3. Find the volume fraction and volume percent of isopropyl alcohol in the solution.

Solution. Volume of solute = 125 cm^3
Volume of solution = 175 cm^3

$\therefore$ Volume fraction $= \frac{125}{175} = 0.714$

Volume percent $= \frac{125}{175} \times 100 = 71.4\%$

Illustraion 8. Calculate volume strength of H_2O_2 in 5L solution which yields 100 L of O_2 at NTP.

Solution 5L H_2O_2 gives = 100 L O_2
1L H_2O_2 gives = 20 L O_2
i.e. 20 V H_2O_2 solution

BEGINNER'S BOX-1

1. What is the normality of 2M H_3PO_2 solution?
(1) 0.5 N (2) 1.0N (3) 2.0 N (4) 3.0 N

2. 23 g ethanol is dissolved in 36 g water. Find mole fraction of ethanol?
(1) 2 (2) 0.5 (3) 0.2 (4) 0.8

3. How many gram of HNO_3 is required to prepare 400 mL solution of 0.2 M HNO_3?
(1) 5.04 g (2) 5040 g (3) 25.2 g (4) 2.52 g

4. Calculate normality of 2.1% (w/V) H_2SO_4 solution?

(1) 2.14 N (2) 4.28 N (3) 0.428 N (4) 0.214 N

5. What is the molarity of 1N H_2SO_4 solution?

(1) 1 M (2) 2M (3) 0.5 M (4) 3M

6. 20.6 g NaBr is dissolved in 500 mL solution what is the molarity of resulting solution?

(1) 0.6 (2) 0.4 (3) 1 (4) None

7. Calculate molality of the solution obtained by dissolving 11.7 g NaCl in 500 g water

(1) 0.1 m (2) 0.3 m (3) 0.2m (4) 0.4m

8. Density of 2.03 M aqueous solution of acetic acid is 1.017 g mL^{-1} molecular mass of acetic acid is 60. Calculate the molality of solution?

(1) 2.27 (2) 1.27 (3) 3.27 (4) 4.27

9. A molar solution is one that contains one mole of solute in

(1) 1000 g of the solvent (2) one litre of the solution
(3) 1000 g of the solution (4) 22.4 litres of the solution

10. Calculate the mole percentage of CH_3OH and H_2O respectively in 60% (by mass) aqueous solution of CH_3OH

(1) 45.8, 54.2 (2) 54.2, 45.8 (3) 50, 50 (4) 60, 40

3.3 SOLUBILITY

Maximum amount of solute which can be dissolved in a specified amount of solvent at constant temperature is solubility. Solubility is affected by nature of solute and solvent as well as by temperature and pressure.

(a) Solubility of Solid in Liquid

Polar solutes are soluble in polar solvent and non polar solutes are soluble in non polar solvent due to similar intermolecular forces.

When solid solutes are dissolved in solvent then following equilibrium exists.

$$\text{Solute + Solvent} \underset{\text{Crystallization}}{\overset{\text{Dissolution}}{\rightleftharpoons}} \text{Solution}$$

Solubility of solids is affected by temperature and pressure according to Le-chatlier's principle. If dissolution is exothermic then solubility decreases with increase in temperature and if endothermic then solubility increases with increase in temperature.

Solubility of solids is not affected by pressure significantly since solids are highly incompressible.

(b) Solubility of Gases in Liquid

Certain gases are highly soluble in water like NH_3, HCl etc. and certain gases are less soluble in water like O_2, N_2, He etc. Solubility of gases is affected by pressure and temperature. Increasing pressure increases solubility and increase in temperature decreases solubility. During dissolution of gas pressure of gas decrease and dissolution of gas is exothermic in nature.

HENRY'S LAW

It can be stated as at constant temperature the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

or

Mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.

or

The partial pressure of the gas in vapour phase (P) is proportional to the mole fraction of the gas (X) in the solution. (This is most common definition)

$P = K_HX$ K_H = Henry's Constant

Henry's Constant is not a universal constant. It depends on nature of gas and temperature. K_H increases with increase in temperature therefore solubility of gas decreases.

Illustrations

Illustraion 9. Henry's Law Constant for CO_2 in water is 1.67×10^8 Pa at 298K. Calculate the quantity of CO_2 in 1 L of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

Solution. $P = K_H X_{gas}$

$$X_{gas} = \frac{P}{K_H} = \frac{2.5 \times 10^5}{1.67 \times 10^8} = 1.5 \times 10^{-3}$$

$$\frac{n}{n+N} = X$$

$$\frac{n}{N} = X \quad \because n << N \therefore n + N \simeq N$$

$$\frac{n}{55.55} = 1.5 \times 10^{-3} = 8.3 \times 10^{-2} \text{ mol L}^{-1}$$

$$= 3.65 \text{ g L}^{-1}$$

3.4 VAPOUR PRESSURE

At a constant temperature, the pressure exerted by the vapours of a liquid on its surface when they (liquid and its vapours) are in equilibrium, is known as vapour pressure.

Factor affecting vapour pressure :

(a) Nature of liquid (b) Temperature

Raoult's Law

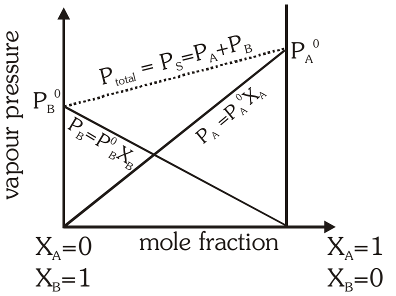
(a) For liquid-liquid system : For a solution of volatile liquids the partial vapour pressure of any component at constant temprature is equal to vapour pressure of pure component multiplied by mole fraction of that component in the solution.

	Liquid (B)	**Liquid (A)**
Vapour pressure in pure state	P_B^0	P_A^0
Partial vapour pressure	P_B	P_A
Mole fraction in solution	X_B	X_A
Moles	n moles	N moles
Mass	w g	W g
Molar mass	m	M

$$P_A \propto X_A \text{ so } P_A = P_A^0 X_A \text{ ...(i)}$$

$$P_B \propto X_B \text{ so } P_B = P_B^0 X_B \text{ ...(ii)}$$

At constant temprature partial vapour pressure of component is directly proportional to mole fraction of component in solution.



According to Dalton's law given below :

- $P_{total} = P_A + P_B + \text{.....}$

$\boxed{P_S = X_A P_A^0 + X_B P_B^0}$; $X_A + X_B = 1$

$P_S = (1-X_B) P_A^0 + X_B P_B^0$

$P_S = P_A^0 - X_B P_A^0 + X_B P_B^0$

$P_S = P_A^0 + X_B (P_B^0 - P_A^0)$

$$\boxed{\begin{array}{cccc} P_S = & P_A^0 + & X_B & (P_B^0 - P_A^0) \\ \downarrow & \downarrow & \downarrow & \downarrow \\ y & c & x & m \end{array}}$$

slope can be positive or negative.

when $P_B^0 > P_A^0$ when $P_A^0 > P_B^0$

- **Dalton's Law**

Partial pressure of gas = mole fraction ×total pressure of gas

$P_A = Y_A P_T$

$P_B = Y_B P_T$

$P_A + P_B = P_T$

$$\boxed{\begin{array}{l} X_A P_A^0 = Y_A P_T \\ X_B P_B^0 = Y_B P_T \end{array}}$$

Y_A and Y_B gives mole fraction in vapour phase

X_A and X_B gives mole fraction in liquid phase.

Illustrations

Illustration 10. Methanol and C_2H_5OH form an ideal solution. Solution is prepared by mixing 32 g of CH_3OH and 23 g of C_2H_5OH at 300K. At 300K $P^0_{methanol}$ = 90 mm of Hg and $P^0_{ethanol}$ = 51 mm of Hg. Calculate

(i) partial vapour pressure of its constitutents and total vapour pressure of solution.

(ii) Mole fraction of each component in vapour phase.

Solution (i) $n_{CH_3OH} = \dfrac{32}{32} = 1$; $n_{C_2H_5OH} = \dfrac{23}{46} = 0.5$

$$X_{CH_3OH} = \frac{1}{1.5} = \frac{2}{3}; \quad X_{C_2H_5OH} = \frac{0.5}{1.5} = \frac{1}{3}$$

$$p_{CH_3OH} = p_m^0 . X_m = 90 \times \frac{2}{3}$$

P_{CH_3OH} = 60 mm of Hg

$$p_{C_2H_5OH} = p_e^0 . X_e = 51 \times \frac{1}{3}$$

$P_{C_2H_5OH}$ = 17 mm of Hg

$$p_S = p_{CH_3OH} + p_{C_2H_5OH}$$

P_S = 77mm of Hg

(ii) $60 = Y_A \times 77$ $\qquad$ $17 = Y_B \times 77$

$$Y_{CH_3OH} = \frac{60}{77} = 0.78 \; ; \qquad Y_{C_2H_5OH} = 0.22$$

(b) **For solid - liquid system** : non-volatile solute (B) and volatile solvent (A)

$$P_B^0 = 0$$

$$P_S = X_A P_A^0 + X_B P_B^0$$

$$\boxed{P_S = X_A P_A^0 = \frac{N}{n+N} P_A^0} \quad \text{...(i)}$$

For solution of non-volatile solute : At constant temperature vapour pressure of solution containing non-volatile solute is proportional to mole fraction of solvent.

$$\therefore \quad P_S \propto \frac{N}{n+N} \quad ; \; X_A + X_B = 1$$

$$P_S = (1-X_B)P^0_A \quad ; \; P_S = P^0_A - X_B P^0_A$$

$$X_B P^0_A = P^0_A - P_S \;\Rightarrow\; \boxed{\frac{P_A^0 - P_S}{P_A^0} = X_B = \frac{n}{n+N}} \quad \text{....(ii)}$$

- When a non-volatile solute is added to a volatile liquid its vapour pressure decrease because less number of solvent particles present in solution at surface. (as compare to pure solvent)

∴ less vapour is formed and vapour pressure of solution decreases

$P^0_A - P_S = \Delta P$ (lowering of vapour pressure)

$\frac{P^0_A - P_S}{P^0_A}$ = relative lowering of vapour pressure.

$$\frac{P^0_A}{P^0_A - P_S} = \frac{n+N}{n} \Rightarrow \frac{P^0_A}{P^0_A - P_S} = 1 + \frac{N}{n}$$

$$\Rightarrow \frac{P^0_A - P^0_A + P_S}{P^0_A - P_S} = \frac{N}{n} \Rightarrow \frac{P_S}{P^0_A - P_S} = \frac{N}{n}$$

$$\Rightarrow \boxed{\frac{P^0_A - P_S}{P_S} = \frac{n}{N}} \quad \ldots\text{(iii)}$$

$$\Rightarrow \Delta P \propto \frac{n}{N}$$

Ex. The vapour pressure of pure liquid A is 40 torr at 310 K. The vapour pressure of this liquid in solution with solid B is 32 torr. Calculate X_A in solution.

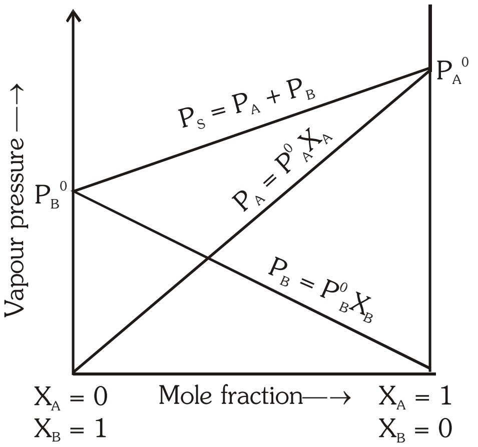
Sol. $32 = X_A \times 40$

$X_A = 0.8$

3.5 IDEAL SOLUTIONS (mixture of two liquids A and B)

- A solution which obeys Raoult's law exactly at all concentrations and at all temperatures is called an ideal solution.
- For ideal solutions; A-A interactions = B-B interactions = A-B interactions.

An ideal solution possesses the following characteristics :



- Volume change on mixing should be zero. $\Delta V_{mix} = 0$, i.e., $(V_{solute} + V_{solvent} = V_{solution})$
- Heat change on mixing should be zero. $\Delta H_{mix} = 0$ (Heat is neither absorbed nor evolved)
- There should be no chemical reaction between liquid A and liquid B.
- Ideal solution must obey Raoult's law at all concentrations.

$$P_A = P^0_A . X_A \,,\; P_B = P^0_B . X_B$$

- observed VP = calculated VP
- observed BP = calculated BP
- $\Delta S_{mix} > 0$
- $\Delta G < 0$

Example

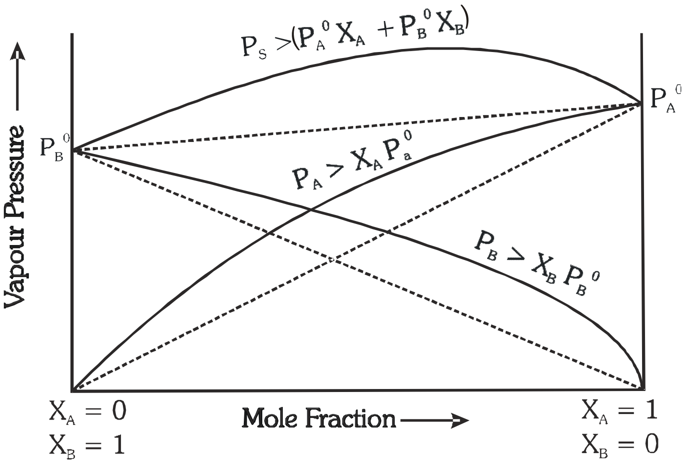
(i) Benzene and toluene
(ii) CCl_4 and $SiCl_4$
(iii) n-hexane and n-heptane
(iv) C_2H_5Br and C_2H_5Cl
(v) PhCl and PhBr
(vi) n-butylchloride and n-butylbromide

3.6 NON-IDEAL SOLUTIONS

- For non ideal solutions ; A–A interactions or B-B interactions ≠ A-B interactions.
- Those solutions which do not obey Raoult's law are called non-ideal solutions.
- For such solutions ; $P_A \neq P_A^o X_A$; $P_B \neq P_B^o X_B$
- Non ideal solutions are formed when the components differ much in their structures and polarities.

  So $\Delta H_{mixing} \neq 0$ and $\Delta V_{mixing} \neq 0$
- Non ideal solutions show either positive or negative deviations from Raoult's law.

(a) Non ideal solutions having positive deviation from Raoult's law.



- In these solutions A-B interactions are less than A-A and B-B molecular interactions.

$$P_A > P_A^o X_A$$

$$P_B > P_B^o X_B$$

- The total vapour pressure of the solution will be greater than the corresponding vapour pressure expected in case of an ideal solution of same composition. i.e.

$$P_{total} > (P_A^o X_A + P_B^o X_B)$$

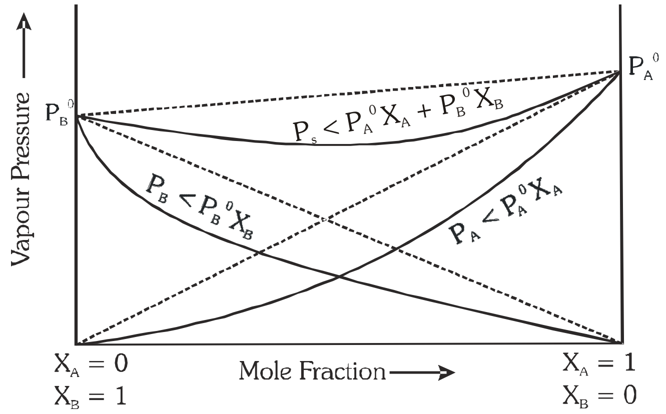
- $\Delta H_{mix} > 0$; endothermic dissolution ; heat is absorbed.
- $\Delta V_{mix} > 0$. ; volume increases after dissolution, i.e., $(V_{solute} + V_{solvent} < V_{solution})$.
- 'A' and 'B' escape easily showing higher vapour pressure than the expected value.

  $(B.P.)_{th} > (B.P.)_{exp}$
- $(\Delta S)_{mix} = +ve$, $\Delta G = -ve$

  Entropy change in mixing is positive.

Examples : (i) Ethanol and cyclohexane
(ii) Ethanol and Water
(iii) Ethanol and Acetone
(iv) Methanol and H_2O
(v) CCl_4 and Benzene
(vi) CCl_4 and Toluene
(vii) CCl_4 and $CHCl_3$
(viii) CCl_4 and Methanol
(ix) Benzene and Acetone
(x) CS_2 and Acetone
(xi) CS_2 and Acetaldehyde

(b) Non ideal solutions having negative deviation from Raoult's Law



- In these solutions the A–B interactions are stronger than the A–A and B–B molecular interactions.

  $P_A < P_A^o X_A \quad ; \quad P_B < P_B^o X_B$

- $P_{total} < (P_A^o X_A + P_B^o X_B)$

  Total vapour pressure is less than sum of individual vapour pressure.
- $\Delta H_{mix} < 0$; exothermic dissolution heat is evolved.
- $\Delta V_{mix} < 0$; volume decreases during dissolution, i.e., $(V_{solute} + V_{solvent} > V_{solution})$.
- Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.

Examples
(i) $CHCl_3$ and CH_3COCH_3
(ii) $CHCl_3$ and C_6H_6
(iii) $CHCl_3$ and $C_2H_5OC_2H_5$
(iv) $CHCl_3$ and HNO_3
(v) $CHCl_3$ and CH_3COOH
(vi) H_2O and HCl
(vii) H_2O and HNO_3
(viii) CH_3COOH and CH_3OH
(ix) CH_3COOH and C_5H_5N
(x) CH_3COCH_3 and Aniline

AZEOTROPIC MIXTURES :

Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature, the liquid and vapour have the same composition, and no further separation occurs.

Components form azeotrope can't be separated by fractional distillation but can be separated by azeotropic distillation.

Solutions showing Positive deviation form minimum boiling azeotrope and solutions showing negative deviation form maximum boiling azeotrope.

There are two types of azeotropes :

(a) Minimum boiling azeotrope (b) Maximum boiling azeotrope

(a) The solutions which show a large positive deviation from Raoult’s law form minimum boiling azeotrope at a specific composition. For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95.57% v/v ethanol.

(b) The solutions that show large negative deviation from Raoult’s law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

GOLDEN KEY POINTS

- Those gases which can react with solvent do not follow Henry's Law. e.g. NH_3 in water.
- Raoult's Law is special case of Henry's Law.
- ΔS is positive and ΔG is negative for ideal as well as non ideal solutions.
- The vapour phase is richer in more volatile component than the less volatile component. This is called as Konowaloff's rule.

Illustrations

Illustraion 11. 1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mole. Octane (V.P. = 31 mm of Hg), form an ideal solution. Find out the vapour pressure of solution.

Solution. Total mole = 1 + 4 = 5

Mole fraction of heptane $X_A = 1/5$

Mole fraction of octane $X_B = 4/5$

$$P_S = X_A P_A^0 + X_B P_B^0 = \frac{1}{5}\times 92 + \frac{4}{5}\times 31 = 43.2 \text{ mm of Hg.}$$

Illustraion 12. At 88^0C benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88^0C at 1 atm pressure (benzene – toluene form an ideal solution).

Solution. P_S = 760 torr, because solution boils at 88^0C

$$P_S = P_B^0 X_B + P_t^0 X_t$$

$\therefore$ 760 = 900 a + 360 – 360 a

a = 0.74 where 'a' is mole fraction of $C_6H_6(X_B)$

BEGINNER'S BOX-2

1. Which of the gas will not follow Henry's law?
(1) HCl (2) He (3) O_2 (4) H_2

2. If solubility of gas 'X' is 0.5 gL^{-1} at 1 bar then its solubility at 3 bar pressure will be
(1) 0.5 gL^{-1} (2) 1.5 gL^{-1} (3) 3.0 gL^{-1} (4) 2 gL^{-1}

3. Among the following that forms an ideal solution?
(1) water and methanol (2) acetone and ethanol (3) benzene and toluene (4) water and HCl

4. On mixing 10 mL of acetone with 40 ml of chloroform the total volume of the solution is
(1) < 50 mL (2) > 50 mL (3) = 50 mL (4) cannot be predicted

5. The mixture of n-hexane and n-heptane is an example of
(1) ideal solution (2) non-ideal solution (3) dilute solution (4) none

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3.7 COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS (CP)

Those physical properties of a solution which depends upon the relative number of particles of solute and do not depend on nature of solute particles are called colligative properties.

CP $\propto$ Number of solute particles

$\propto$ Number of molecules (in the solution of non electrolyte)

$\propto$ Number of ions (in the solution of electrolytes)

$\propto$ Number of moles of solute

$\propto$ Mole fraction of solute

The following four properties are CP :

(a) Relative lowering in vapour pressure of solvent
(b) Elevation in boiling point (ΔT_b) of solvent
(c) Depression in freezing point (ΔT_f) of solvent
(d) Osmotic pressure (π or P) of solution

(a) Relative Lowering in Vapour Pressure

- When a nonvolatile solute is dissolved in a pure solvent, the vapour pressure of the solvent is lowered i.e. the vapour pressure of a solution is always lower than that of pure solvent, because the escaping tendency of solvent molecules decreases (due to lesser solvent molecules per unit surface area).

  If at a certain temperature P° is the vapour pressure of pure solvent, and P_s is the vapour pressure of solution then

  According to Raoult's law :

  Relating lowering in vapour pressure = $\dfrac{P_A^0 - P_S}{P_A^0} = \dfrac{n_B}{N_A + n_B}$

  For a dilute solution $n_B << n_A$ $\quad \therefore \dfrac{P_A^0 - P_S}{P_A^0} \approx \dfrac{n_B}{N_A}$ so $\Delta P \propto \dfrac{n_B}{N_A}$

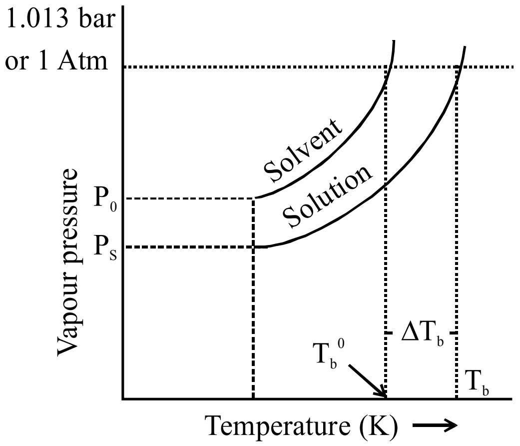
- Relative lowering depends upon relative number of solute particles. Therefore it is called colligative properties.

(b) Elevation in Boiling Point

- The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure.
- When a non-volatile solute is dissolved in a pure solvent, its vapour pressure is decreased and boiling point increases. The difference of boiling points of the solution and pure solvent is called elevation in boiling point.(ΔT_b)
- If T^0_b is the boiling point of pure solvent and T_b is the boiling point of the solution then, $T_b > T^0_b$ and the elevation in boiling point $\Delta T_b = T_b - T^0_b$
- The elevation in boiling point (ΔT_b) is directly proportional to lowering of vapour pressure of the solution i.e.

  $\Delta T_b \propto (P^\circ - P_s)$ from graph and

  $$\Delta T_b \propto \Delta P \propto \frac{n_B}{N_A}$$



T_b = Boiling point of solution
T_b^0 = Boiling point of solution

The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.

$$\therefore \quad \Delta T_b \propto \frac{n_B}{N_A} = \frac{w_B M_A}{m_B W_A} \text{ for a solvent } P^0 \ \& \ M_A = \text{constant}$$

$$\therefore \quad \Delta T_b \propto \frac{w_B}{m_B W_A} \text{ or } \Delta T_b = \frac{K w_B}{m_B W_A}$$

where K = elevation constant

if $\dfrac{w_B}{m_B} = 1$ mole and $W_A = 1$ g

then $\Delta T_b = K$ (Elevation constant or molecular elevation constant) if $\frac{w_B}{m_B} = 1$ and $W_A = 1000$ gram; Then $\Delta T_b = K_b$(molal elevation constant)

$\therefore \frac{K}{1000} = K_b$ (molal elevation constant or Ebullioscopic constant)

$$\Delta T_b = \frac{K_b \times w_B \times 1000}{m_B \times W_A}; \qquad \Delta T_b = \frac{w_B}{m_B} \times \frac{1000}{W_A} \times K_b$$

$\therefore \boxed{\Delta T_b = \text{molality} \times K_b}$ $\quad \therefore \Delta T_b \propto$ molality

hence elevation in boiling point (ΔT_b) is a colligative property.

- K_b depends only on nature of solvent which can be explained by thermodynamic relation.

$$\boxed{K_b = \frac{RT_b^{0^2}}{1000 L_v} = \frac{M_w RT_b^{0^2}}{1000 \Delta H_{vap}}}$$

Where T_b^0 = Boiling point of solvent.

M_w = Molar mass of solvent.

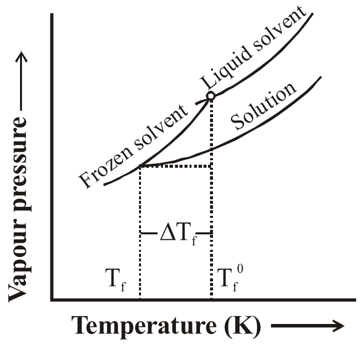
ΔH_{vap} = Enthalpy of vapoursation per mole of solvent

L_v = Latent heat of vapourisation per gram of solvent

- **The molal elevation constant for some common solvents are given in the following table**

Solvent	**B.P. (^{0}C)**	**Molal elevation constant (K_b)**
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.63
Carbon tetra chloride	76.8	5.03
Benzene	80.0	2.53
Ethyl alcohol	78.4	1.20

(c) Depression in Freezing Point



- The freezing point of a liquid is that temperature at which the liquid and its solid state exist in equilibrium with each other.
- It may be defined as the temperature at which the liquid and solid states of a substance have the same vapour pressure.
- When a non-volatile is dissolved in a pure solvent the vapour pressure of the solvent is lowered.
- If T^0_f is the freezing point of pure solvent and T_f is the freezing point of its solution then, $T_f < T^0_f$
- The difference in the freezing point of pure solvent and solution is called depression of freezing point (ΔT_f)

  $\Delta T_f = T^0_f - T_f$; the depression in freezing point is directly proportional to lowering in vapour pressure (ΔP)

  $$\Delta T_f \propto \Delta P \propto \frac{n_B}{N_A}; \quad \Delta T_f \propto \frac{n_B}{N_A} \quad \text{so} \quad \boxed{\Delta T_f = K_f \times \text{molality}}$$

  K_f = molal depression constant or Cryoscopic constant.

- K_f depends only on nature of solvent which can be explained by thermodynamic relation

$$\boxed{K_f = \frac{RT_f^{0^2}}{1000 L_f} = \frac{RT_f^{0^2} M_w}{1000 \Delta H_f}}$$

Where T^0_f = Freezing point of solvent

M_w = Molar mass of solvent

ΔH_f = Enthalpy of fusion per mole of solvent

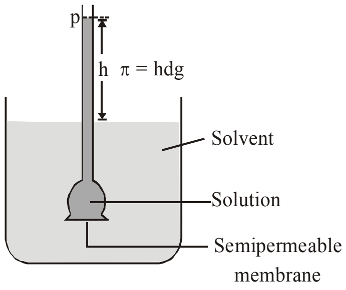
L_f = latent heat of fusion per gram of solvent

- **The molal depression constant for some common solvents are given in the following table**

Solvent	F.P.(^{0}C)	Molal depression constant (K_f)
Water	0.0	1.86
Ethyl alcohol	– 114.6	1.99
Chloroform	– 63.5	4.79
Carbon tetra chloride	– 22.8	31.80
Benzene	5.5	5.12
Camphor	179.0	39.70

(d) Osmosis and Osmotic Pressure

Osmosis : Osmosis is defined as the spontaneous net flow of solvent molecules through semipermeable membrane from a solvent to a solution or from a dilute solution to a concentrated solution.



Level of solution rises in the thistle funnel due to osmosis of solvent

Osmotic Pressure (p or π)

- The external pressure which must be applied on the solution in order to stop the flow of solvent into the solution through semipermeable membrane is equal to osmotic pressure

or

- Hydrostatic pressure developed in a vertical column when solution and solvent are separated by SPM.

Osmotic pressure = hydrostatic pressure ; $\boxed{\pi = hdg}$

where h = increase in level in the tube of unit cross section

d = density of solution

g = acceleration due to gravity

Van't Hoff law for Dilute Solution

According to it Gas equation PV = nRT is also followed by dilute solution when pressure of gas is replaced by osmotic pressure of solution.

$$\boxed{\begin{array}{c} PV = nRT \\ \downarrow\downarrow\quad\downarrow \\ \pi V = nRT \end{array}}$$

π = osmotic pressure of solution (atm)

V = volume of solution (L)

n = moles of solute

R = (S) gas constant / solution constant = 0.0821 L atm $mol^{-1}K^{-1}$; 0.083 L bar $mol^{-1}K^{-1}$

$$\pi = \left(\frac{n}{V}\right)RT \qquad \boxed{\pi = CRT}$$

At constant temperature $\pi \propto C$ $\therefore$ π is a colligative property.

- On the basis of osmotic pressure solution can be classified by following ways :

(i) **Isotonic solutions :** Solutions having same osmotic pressure are called isotonic solution.

$\boxed{\pi_1 = \pi_2}$; primary condition

$C_1RT = C_2RT$ (at same temperature)

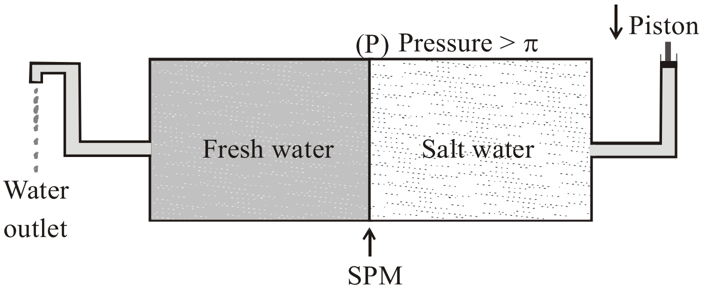
$\boxed{C_1 = C_2}$ (secondary condition) ; means

$\frac{n_1}{V_1} = \frac{n_2}{V_2}$; such solutions are known as **isotonic**

(ii) $\pi_1 > \pi_2$ or $C_1 > C_2$ then solution 1 is called **hypertonic** and solution 2 is called **hypotonic**

Reverse Osmosis

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. Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.



Illustrations

Illustraion 13. The vapour pressure of benzene at 90⁰C is 1020 torr. A solution of 5 g of a solute in 58.5 g benzene has vapour pressure 990 torr. The molecular weight of the solute is?

Solution. $\frac{P^0 - P_S}{P_S} = \frac{w \times M}{m \times W} \Rightarrow \frac{1020 - 990}{990} = \frac{5 \times 78}{m \times 58.5} \Rightarrow m = 220$

Illustraion 14. A 5% $\left(\frac{w}{V}\right)$ solution of cane sugar is isotnic with 0.877% $\left(\frac{w}{V}\right)$ solution of unknown solute. Find out molecular weight of unknown solute.

Solution $\frac{5 \times 10}{342} = \frac{0.877 \times 10}{x}$

$x = \frac{0.877 \times 342}{5}$

$x = 0.877 \times 68.4 = 60$

Illustraion 15. 0.15 g of a substance dissolved in 15 g of solvent boiled at a temperature higher by 0.216 °C than that of the pure solvent. What is the molar mass of the substance. [K_b for solvent = 2.16 $°Cm^{-1}$]

Solution. Given $K_b = 2.16^0C$, $w = 0.15$ g, $\Delta T_b = 0.216^0C$, $W = 15$ g

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

$$\Delta T_b = \frac{w}{m \times W} \times 1000 \times K_b \Rightarrow 0.216 = \frac{0.15}{m \times 15} \times 1000 \times 2.16$$

$$\Rightarrow \quad m = \frac{0.15 \times 1000 \times 2.16}{0.216 \times 15} = 100$$

Illustraion 16. The rise in boiling point of a solution containing 1.8 g glucose in 100 g of a solvent is 0.1^0C. The molal elevation constant of the liquid is –

Solution. $\Delta T_b = \text{Molality} \times K_b$

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

given $\Delta T_b = 0.1^0C$, $m = 180$, $W = 100$, $w = 1.8$

$$K_b = \frac{180 \times 0.1 \times 100}{1000 \times 1.8} = 1.0\ °Cm^{-1}$$

Illustraion 17. If freezing point of a solution prepared from 1.25 g of a non electrolyte and 20 g of water is 271.9 K, the molar mass of the solute will be

Solution. Given : $(T_f)_s = 271.9$ K, $w = 1.25$ g, $W = 20$ g, $K_f = 1.86$ K kg mol^{-1}

$\Delta T_f = T_b^0 - (T_f)_s = 273 - 271.9 = 1.1$

$\Delta T_f = \text{Molality} \times K_f$ or $\Delta T_f = \dfrac{w}{m \times W} \times 1000 \times K_f$

$$m = \frac{w \times 1000 \times K_f}{\Delta T_f \times W} = \frac{1.25 \times 1000 \times 1.86}{1.1 \times 20} = 105.68$$

Illustraion 18. Molal depression constant for water is 1.86 $°Cm^{-1}$. The freezing point of a 0.05 molal solution of a non electrolyte in water is –

Solution.

$\Delta T_f = \text{Molality} \times K_f = 0.05 \times 1.86 = 0.093^0C$

$(T_f)_S = T_0 - 0.093 = 0 - 0.093$

$(T_f)_S = -0.093°C$

Illustraion 19. A cane sugar solution has an osmotic pressure of 2.46 atm at 300 K. What is the strength of the solution.

Solution. $\pi V = nST$ or $\pi = \dfrac{n}{V} ST = CST$ or $C = \dfrac{\pi}{ST} = \dfrac{2.46}{300 \times 0.0821} = 0.1$ M

Illustraion 20. What is the osmotic pressure of 12% solution of cane sugar (molecular weight 342) at 17 °C.

Solution. 12 g sugar is dissolved in 100 mL

thus 342 g sugar is dissolved in $\dfrac{100 \times 342}{12 \times 1000} = 2.85$ L

Now $\pi V = RT$ $\{\because\ n = 1\}$

$$\pi = \frac{RT}{V} = \frac{0.0821 \times 290}{2.85} = 8.35 \text{ atm}$$

Illustraion 21. A solution containing 8.6 g urea in one litre was found to be isotonic with 0.5% (weight/volume) solution of an organic, non-volatile solute. Calculate molar mass organic compound.

Solution. Solutions are isotonic

so $\pi_1 = \pi_2$ or $\frac{n_1}{V_1}RT = \frac{n_2}{V_2}RT$ { R & T are constant}

so, $\frac{n_1}{V_1} = \frac{n_2}{V_2}$ or $\left(\frac{w_1}{m_1 \times v_1}\right)_{urea} = \left(\frac{w_2}{m_2 \times v_2}\right)_{organic}$

or $\frac{8.6}{60 \times 1000} = \frac{0.5}{m_2 \times 100}$ $\Rightarrow$ $m_2 = 34.89$

GOLDEN KEY POINTS

- (i) $\frac{\Delta P}{P^0} \approx \frac{n}{N} \Rightarrow \Delta P = \frac{wM}{mW} \times P^0$ (ii) $\Delta T_b = \left(\frac{w \times 1000}{m \times W}\right)K_b$ (iii) $\Delta T_f = \left(\frac{w \times 1000}{m \times W}\right)K_f$ (iv) π=CRT
- Best method to determine molecular weight of biomolecules like protein and polymers is osmotic presure. Because it is a colligative property also as no temprature change is involved so there is no chance of change in nature of biomolecule. In other methods changes are very less and it is difficult to measure very small changes accurately. But osmotic pressure can be easily measured at room temperature at which biomolecules remain in original state.
- 0.91% $\left(\frac{w}{V}\right)$ NaCl solution is isotonic with blood.
- Intravenous injections need to be isotonic with blood to prevent damage to RBC.
- Magnitude of osmotic pressure is independent with the nature of solvent.
- Berkley Hartley's method and Funnel experiment (π = hdg) are used to determine osmotic pressure.
- Ostwalds process is used to determine elevation in boiling point.
- Camphor is the best solvent for determination of molar mass of solute by using depression in freezing point since its K_f is very high.

BEGINNER'S BOX-3

1. An example of colligative property
(1) freezing point (2) boiling point (3) vapour pressure (4) osmotic pressure

2. The freezing point order of the solution of glucose is
(1) 10% > 3% > 2% > 1% (2) 1% > 2%> 3%> 10%
(3) 1% > 3% > 10% > 2% (4) 10% > 1% > 3% > 2%

3. In cold countries, ethylene glycol is added to water in the radiators of cars during winters. It result in reducing
(1) viscoity (2) specific heat (3) freezing point (4) boiling point

4. Calcualte the molal depression constant of a solvent, which has freezing point 16.6 °C and latent heat of fusion 180.75 Jg^{-1}
(a) 2.68 (2) 3.86 (3) 4.68 (4) 2.86

5. The osmotic pressure of a solution at 0 °C is 4 atm. What will be its osmotic pressure at 546 K under similar condition?
(1) 4 atm (2) 2 atm (3) 8 atm (4) 1 atm

3.8 ABNORMAL COLLIGATIVE PROPERTIES

- It has been observed that difference in the observed and calculated molecular masses of solute is due to association or dissociation of solute molecules in solution. It results in a change in the number of particles in solution.
- **Van't hoff factor (i)** : Tells about relationship between normal colligative properties and abnormal colligative properties.
- $$i = \frac{\text{number of particles after dissociation or association}}{\text{number of particles before dissociation or association}} = \frac{\text{observed colligative properties}}{\text{calculated colligative properties}}$$
$$= \frac{\text{calculated molecular mass}}{\text{observed molecular mass}}$$
- If $i = 1$ Neither dissociation nor association ; Ex. glucose, urea, sugar
- if $i > 1$ Dissociation will occur ; Ex. NaCl, KCl, $BaCl_2$
- if $i < 1$ Association will occur ; Ex. CH_3COOH, PhCOOH in benzene

CASE I :

DISSOCIATION OF SOLUTE : Molecules of electrolytes undergo ionization or dissociation in polar solvents to give two or more particles in solution. This dissociation results in an increase in the total number of particles, and therefore the value of colligative properties of such solutions will be higher. As the colligative properties are inversely related to molecular weight, so the molecular weight of ionizable solute will be less than the theoretical value.

Number of solute particles in solution increses.

- observed / experimental C.P. > calculated C.P. (normal)
- observed /experimental molecular weight of solute < calculated (normal) moleclar weight of solute

$$\therefore \text{ C.P.} \propto \frac{1}{\text{molecular weight of solute}}$$

- Calculation of 'i' : Let solute be A_xB_y (electrolyte)

$$\mathbf{A_xB_y \rightarrow xA^{y+} + yB^{x-}} \quad ; \quad x + y = n \text{ (total number of ions)}$$

	A_xB_y	xA^{y+}	yB^{x-}
Initially	1 mol	0	0
After dissociation	$(1-\alpha)$	$x\alpha$	$y\alpha$

Total number of solute particles $= 1-\alpha + x\alpha + y\alpha$
$= 1 - \alpha + (x+y)\alpha$
$= (1-\alpha + n\alpha)$mol

Observed colligative property is proportional to observed number of solute particles $(1-\alpha + n\alpha)$

$$i = \frac{\text{number of particles after dissociation}}{\text{number of particles before dissociation}} = \frac{1-\alpha+n\alpha}{1}$$

$$\boxed{i = 1 + (n-1)\alpha}$$

where α is the degree of dissociation

- For strong electrolytes

if $\alpha=1$ or 100% $\Rightarrow$ then $\boxed{i = n}$

Ex. NaCl $\Rightarrow$ i =2; α = 100%
$K_2SO_4 \Rightarrow$ i = 3 α = 100%

Ex. $K_4[Fe(CN)_6] \Rightarrow$ i =5 for α = 100%
For α = 50% $i = 1 + (n-1)\alpha$
i =3

CASE II :

ASSOCIATION OF SOLUTE : The formation of a bigger molecule by the union of two, three or more solute molecules is called association. As a result, the total number of particles in solution becomes less than the number of molecules initially dissolved in the solution and hence the colligative properties will have lower value. As the molar mass of solute is inversely proportional to the colligative properties, so the molar mass of solute will be greater than theoretical value.

Number of solute particles in solution decreases.

- Observed /experimental C.P. < calculated C.P.
- Observed / experimental molecular weight of solute > normal molecular weight of solute

$$\therefore \ \text{C.P.} \propto \frac{1}{\text{Molecular weight of solute}} \quad ; \qquad i < 1 \text{ for association.}$$

- Calculation of i

$$\begin{array}{lll} & \mathbf{nA} \longrightarrow & \mathbf{[A]_n} \\ \text{Initially} & 1 & 0 \\ \text{After association} & (1-\alpha) & \dfrac{\alpha}{n} \end{array}$$

Total number of solute particles = $\left(1-\alpha+\dfrac{\alpha}{n}\right)$ mol

Observed $\text{C.P.} \propto$ observed number of solute particles $\left(1-\alpha+\dfrac{\alpha}{n}\right)$

$$\text{Van't hoff factor (i)} = \frac{\text{number of particles after association}}{\text{number of particle before association}} \ ; \ i = \frac{1-\alpha+\dfrac{\alpha}{n}}{1}$$

$$\boxed{i = 1-\alpha+\frac{\alpha}{n}}$$

α = degree of association

n = number of solute particles which are associated.

- If α = 100% or 1 or α is not specified $\boxed{i = \dfrac{1}{n}}$

Illustrations

Illustraion 22. A 5% solution of anhydrous $CaCl_2$ at 0^0C developed 15 atm osmotic pressure. What is the degree of dissociation of $CaCl_2$?

Solution. 5 g. of $CaCl_2$ are present in 100 mL, so 111 g (M_W of $CaCl_2$) will be present in $\dfrac{100 \times 111}{5 \times 1000} = 2.22$ L

$$\text{Now} \quad \pi V = ST \ \{\because \ n = 1\} \quad \text{or} \quad \pi = \frac{0.082 \times 273}{2.22} = \frac{22.47}{2.22} = 10.09 \text{ atm}$$

$$\text{We know that Van't Hoff factor } i = \frac{\text{observed colligative property}}{\text{Normal colligative property}} = \frac{15}{10.09}$$

$$\text{and} \quad \alpha = \frac{i-1}{n-1} \quad \text{or} \quad \alpha = \frac{\dfrac{15}{10.09}-1}{3-1} = \frac{4.91}{10.09 \times 2} = 0.2433 \ \text{ or } \ 24.33\%$$

Illustraion 23. Calculate the osmotic pressure of 20% (wt/Vol.) anhydrous $CaCl_2$ solution at 0°C assuming 100% ionisation.

Solution

	$CaCl_2$	$\longrightarrow$	Ca^{2+}	+	$2Cl^-$
Before dissociation	1		0		0
After dissociation	$1 - \alpha$		α		2α

Given, w = 20 g, V = 100 mL, T = 273 K,

mol, wt. of $CaCl_2$ = 111

$$\pi_{\text{Normal}} = \frac{w}{mV} \times S \times T = \frac{20 \times 1000 \times 0.0821 \times 273}{111 \times 100} = 40.38 \text{ atm.}$$

Now, $$i = \frac{1+2\alpha}{1} = 1 + 2 = 3 \ (\because \alpha = 1)$$

$$\pi_{\text{exp}} = i \times \pi_{\text{Normal}}$$

$$\therefore \quad \pi_{\text{exp}} = 40.38 \times 3 = 121.14 \text{ atm}$$

BEGINNER'S BOX-4

1. Calculate the percentage degree of dissociation of an electrolyte AB_2(normal molar mass = 164) in H_2O if observed molar mass is 65.6

(1) 50% (2) 25% (3) 75% (4) None

2. Which of the following solution will have highest freezing point

(1) 1M urea (2) 1M Na_2SO_4 (3) 1M NaCl (4) 1M $Al_2(SO_4)_3$

3. A 1.17% solution of NaCl is isotonic with 7.2% solution of glucose calculate the value of i of NaCl

(1) 1 (2) 2 (3) 3 (4) 4

4. Van't hoff factor of Hg_2Cl_2 in its aqueous solution will be (Hg_2Cl_2 is 80% ionized in the solution)

(1) 1.6 (2) 2.6 (3) 3.6 (4) 4.6

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	3	1	3	3	2	4	1	2	1

BEGINNER'S BOX-2	Que.	1	2	3	4	5					
	Ans.	1	2	3	1	1					

BEGINNER'S BOX-3	Que.	1	2	3	4	5					
	Ans.	4	2	3	2	3					

BEGINNER'S BOX-4	Que.	1	2	3	4						
	Ans.	3	1	2	2						

EXERCISE-I (Conceptual Questions) Build Up Your Understanding

CONCENTRATION TERMS

1. 8 g NaOH is dissolved in one litre of solution, its molarity is :
(1) 0.8 M (2) 0.4 M (3) 0.2 M (4) 0.1 M

2. If 18 g of glucose is present in 1000 g of solvent, the solution is said to be :
(1) 1 molar (2) 0.1 molar
(3) 0.5 molar (4) 0.1 molal

3. The molarity of a solution of sodium chloride (mol wt. = 58.5) in water containing 5.85 g of sodium chloride in 500 mL of solution is :-
(1) 0.25 (2) 2.0 (3) 1.0 (4) 0.2

4. For preparing 0.1 M solution of H_2SO_4 in one litre, we need H_2SO_4 :
(1) 0.98 g (2) 4.9 g
(3) 49.0 g (4) 9.8 g

5. Mole fraction of glycerine($C_3H_5(OH)_3$) in a solution of 36 g of water and 46 g of glycerine is :
(1) 0.46 (2) 0.36
(3) 0.20 (4) 0.40

6. 1000 g aqueous solution of $CaCO_3$ contains 10 g of calcium carbonate, concentration of the solution is :
(1) 10 ppm (2) 100 ppm
(3) 1000 ppm (4) 10,000 ppm

7. What is the normality of 1M H_3PO_4 solution ?
(1) 0.5 N (2) 1.0 N
(3) 2.0 N (4) 3.0 N

8. The molarity of 0.2 N Na_2CO_3 solution will be :
(1) 0.05 M (2) 0.2 M
(3) 0.1 M (4) 0.4 M

9. Normality of 0.3 M phosphorous acid is:-
(1) 0.15 (2) 0.6
(3) 0.9 (4) 0.1

10. The molarity of pure water is :
(1) 100 M (2) 55.5 M
(3) 50 M (4) 18M

11. Molarity of 720 g of pure water -
(1) 40M
(2) 4M
(3) 55.5M
(4) Can't be determined

12. Equal weight of NaCl and KCl are dissolved separately in equal volumes of solutions then molarity of the two solutions will be –
(1) Equal
(2) That of NaCl will be less than that of KCl
(3) That of NaCl will be more than that of KCl Solution
(4) That of NaCl will be half of that of KCl solution

13. The mole fraction of oxygen in a mixture of 7g of nitrogen and 8g of oxygen is :
(1) $\frac{8}{15}$ (2) 0.5 (3) 0.25 (4) 1.0

14. In a solution of 7.8 g benzene (C_6H_6) and 46.0g toluene ($C_6H_5CH_3$) the mole fraction of benzene is:-
(1) $\frac{1}{6}$ (2) $\frac{1}{5}$ (3) $\frac{1}{2}$ (4) $\frac{1}{3}$

15. An X molal solution of a compound in benzene has mole fraction of solute equal to 0.2. The value of X is:-
(1) 14 (2) 3.2 (3) 1.4 (4) 2

16. Mole fraction of ethanol in ethanol water mixture is 0.25. Hence percentage concentration of ethanol by weight of mixture is :–
(1) 25% (2) 75% (3) 46% (4) 54%

17. A 500 g tooth paste sample has 0.02 g fluoride concentration. What is the concentration of fluorine in terms of ppm level:-
(1) 250 (2) 40 (3) 400 (4) 1000

18. The normality of 10 mL of a '20 V' H_2O_2 solution is
(1) 1.79 (2) 3.58 (3) 60.86 (4) 6.086

19. 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:-
(1) 0.15 M (2) 1.5 M
(3) 3.0 M (4) 3.4 M

20. Normality of 10% (w\V) H_2SO_4 solution is nearly
(1) 0.1 (2) 0.2 (3) 0.5 (4) 2

21. What volume of 0.1 N HNO_3 solution can be prepared from 6.3 g of HNO_3 ?
(1) 1 litre (2) 2 litre (3) 0.5 litre (4) 5 litre

22. A molal solution is one that contains one mole of a solute in

(1) 1000 g of the solvent
(2) one litre of the solution
(3) one litre of the solvent
(4) 22.4 litres of the solution

23. Which of the following statement is true :-

(a) Molarity is the no. of moles of solute dissolved per litre of solvent.
(b) The molarity and normality of a solution of sodium carbonate are same.
(c) Molality (m) of a solution is defined as the number of moles of solute dissolved is 1000 gm of solution
(d) The ratio of mole fraction of solute and solvent is in the ratio of there respective moles.

(1) a & c
(2) a & d
(3) b & c
(4) Only d

24. Two bottles of A and B contains 1M and 1m aqueous solution $(d \simeq 1 g mL^{-1})$ of sulphuric acid respectively-

(1) A is more concentrated than B
(2) B is more concentrated than A
(3) Concentration of A = concentration of B
(4) It is not possible to compare the concentration

25. Molar concentration of a solution in water is :

(1) Always equal to normality
(2) More than molality of the solution
(3) Equal to molality of the solution
(4) Less than the molality of the solution

26. The molarity of 98% H_2SO_4 (d = 1.8 g mL^{-1}) by wt. is

(1) 6 M
(2) 18 M
(3) 10 M
(4) 4 M

SOLUBILITY (HENRY'S LAW)

27. Henry's law constant for dissolution of CH_4 in benzene at 298 K is 2×10^5 mm of Hg. Then solubility of CH_4 in benzene at 298 K under 760 mm of Hg is :

(1) 1.2×10^{-5}
(2) 3.8×10^{-3}
(3) 4×10^{-7}
(4) 1×10^{-2}

28. Which of the followнig gas does not obey Henrys's law ?

(1) NH_3
(2) H_2
(3) O_2
(4) He

VAPOUR PRESSURE (LIQUID-LIQUID MIXTURE)

29. 1 mol of heptane (V. P. = 92 mm of Hg) was mixed with 4 mol of octane (V. P. = 31mm of Hg). The vapour pressure of resulting ideal solution is :

(1) 46.2 mm of Hg
(2) 40.0 mm of Hg
(3) 43.2 mm of Hg
(4) 38.4 mm of Hg

30. At 88 °C benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will boil at 88 °C at 1 atm. pressure, benzene - toluene form an ideal solution :

(1) 0.416
(2) 0.588
(3) 0.688
(4) 0.740

31. If P_A^0 and P_B^0 are 108 and 36 torr respectively. What will be the mole fraction of A is vapour phase if B has mole fraction in solution 0.5.

(1) 0.25
(2) 0.75
(3) 0.60
(4) 0.35

32. What is correct relation between mole fraction in vapour phase (Y_A) of A in terms of X_A. If mole fraction in solution of A is (X_A) (If P_A^0 is vapour pressure of A in pure state)

(1) $(1-X_A)P_A^0$
(2) $\frac{X_A}{1-X_A}P_A^0$
(3) $\frac{1-X_A}{X_A}P_A^0$
(4) $\frac{P_A^0 X_A}{P_S}$

IDEAL AND NON-IDEAL SOLUTIONS

33. Which condition is not satisfied by an ideal solution

(1) ΔH mixing = 0
(2) ΔV mixing = 0
(3) ΔS mixing = 0
(4) Obeyance of Raoult's law

34. Among the following, that does not form an ideal solution is :

(1) C_6H_6 and $C_6H_5CH_3$
(2) C_2H_5Cl and C_6H_5OH
(3) C_6H_5Cl and C_6H_5Br
(4) C_2H_5Br and C_2H_5I

35. An azeotropic mixture of two liquids has b.p. lower than either of them when it :-
(1) shows a (+ve) deviation from Raoult's law
(2) shows no deviation from Raoult's law
(3) shows (+ve) deviation from Henry's law
(4) shows (–ve) deviation from Henry's law

COLLIGATIVE PROPERTIES

36. Which is not a colligative property ?
(1) Osmotic pressure
(2) Relative lowering in vapour pressure
(3) Depression in freezing point
(4) Refractive index

37. The lowering of vapour pressure of a solvent by addition of a non-volatile solute to it is directly proportional to :
(1) The strength of the solution
(2) The nature of the solute in the solution
(3) The atmospheric pressure
(4) All

38. The relative lowering of vapour pressure is equal to the mole fraction of the nonvolatile solute, This statement was given by :
(1) Raoult (2) Henry (3) Joule (4) Dalton

39. Which one of the following is the incorrect form of Raoult's law
(1) $\frac{P_s}{P^0} = \frac{N}{n+N}$ (2) $\frac{P^0}{P^0 - P_s} = 1 + \frac{N}{n}$
(3) $\frac{P^0 - P_s}{P_s} = \frac{n}{n+N}$ (4) $\frac{P_s}{P^o - P_s} = \frac{N}{n}$

40. The vapour pressure of a solution having solid as solute and liquid as solvent is :
(1) Directly proportional to mole fraction of the solvent
(2) Inversely proportional to mole fraction of the solvent
(3) Directly proportional to mole fraction of the solute
(4) Inversely proportional to mole fraction of the solute

41. If P_0 and P_S are the vapour pressure of solvent and its solution respectively. N_1 and N_2 are the mole fraction of solvent and solute respectively then :
(1) $P_S = \frac{P_0}{N_2}$ (2) $P_0 - P_S = P_0N_2$
(3) $P_S = P_0N_2$ (4) $\frac{(P_0 - P_S)}{P_S} = \frac{N_1}{(N_1 + N_2)}$

42. One mol of non volatile solute is dissolved in two mol of water. The vapour pressure of the solution relative to that of water is
(1) $\frac{2}{3}$ (2) $\frac{1}{3}$ (3) $\frac{1}{2}$ (4) $\frac{3}{2}$

43. The vapour pressure of a dilute aqueous solution of Glucose is 750 mm of mercury at 373 K. The mole fraction of solute is :
(1) $\frac{1}{10}$ (2) $\frac{1}{7.6}$ (3) $\frac{1}{35}$ (4) $\frac{1}{76}$

44. The vapour pressure of water at room temperature is 23.8 mm of Hg. The vapour pressure of an aqueous solution of sucrose with mole fraction 0.1 is equal to :
(1) 23.9 mm Hg (2) 24.2 mm Hg
(3) 21.42 mm Hg (4) 31.44 mm Hg

45. The vapour pressure of pure A is 10 torr and at the same temperature when 1 g of B is dissolved in 20 gm 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 :
(1) 100 amu (2) 90 amu
(3) 75 amu (4) 120 amu

46. The boiling point of C_6H_6, CH_3OH, $C_6H_5NH_2$ and $C_6H_5NO_2$ are 80°C, 65°C, 184°C and 212°C respectively. Which will show highest vapour pressure at room temperature :
(1) C_6H_6 (2) CH_3OH
(3) $C_6H_5NH_2$ (4) $C_6H_5NO_2$

47. If Raoult's law is obeyed, the vapour pressure of the solvent in a solution is directly proportional to :
(1) Mole fraction of the solvent
(2) Mole fraction of the solute
(3) Mole fraction of the solvent and solute
(4) The volume of the solution

48. 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 vapour pressure of the solution is 84 torr at 27°C. The vapour pressure of pure liquid B at 27°C is -
(1) 14 (2) 56 (3) 140 (4) 70

49. The boiling point of an aqueous solution of a non volatile solute is 100.15 °C. What is the freezing point of an aqueous solution obtained by diluting the above solution with an equal volume of water ? The values of K_b and K_f for water are 0.512 and 1.86 K $molality^{-1}$:
(1) –0.544 °C (2) –0.512 °C
(3) –0.272 °C (4) –1.86 °C

50. The molal elevation constant is the ratio of the elevation in B.P. to :

(1) Molarity

(2) Molality

(3) Mole fraction of solute

(4) Mole fraction of solvent

51 Elevation in boiling point was 0.52 °C when 6 g of a compound **x** was dissolved in 100 g of water. Molecular weight of **x** is :(K = 5.2 K mol^{-1} 100 g H_2O)

(1) 120 (2) 60 (3) 100 (4) 342

52. An aqueous solution containing 1g of urea boils at 100.25 °C. The aqueous solution containing 3g of glucose in the same volume will boil at -

(1) 100.75 °C (2) 100.5 °C

(3) 100 °C (4) 100.25 °C

53. Pure benzene freezes at 5.45 °C at a certain place but a 0.374 m solution of tetrachloroethane in benzene freezes at 3.55 °C. The K_f for benzene is-

(1) 5.08 K Kg mol^{-1} (2) 508 K Kg mol^{-1}

(3) 0.508 K Kg mol^{-1} (4) 50.8 °C Kg mol^{-1}

54. An aqueous solution freezes at – 0.186 °C (K_f = 1.86 K kg mol^{-1} ; K_b = 0.512 K kg mol^{-1}). What is the elevation in boiling point ?

(1) 0.186 (2) 0.512

(3) $\frac{0.512}{1.86}$ (4) 0.0512

55. Camphor is used as solvent to determine the molecular weight of nonvolatile solute by Rast method because for camphor -

(1) Molal depression constant is high

(2) Melting point is high

(3) Being cheap

(4) All

56. In the depression of freezing point experiment, it is found that :-

(1) The vapour pressure of solution is more than of pure H_2O.

(2) The vapour pressure of solution is less than that of pure solute

(3) Only solute molecules solidify at of freezing point

(4) Only solvent molecules solidify at freezing point

57. Molal depression constant of water is 1.86 K Kg mol^{-1}. 0.02 mol of urea dissolved in 100 g of water will produce a depression in freezing point of :

(1) 0.186 °C (2) 0.372 °C

(3) 1.86 °C (4) 3.72 °C

58. What would be the freezing point of aqueous solution containing 18 g of $C_6H_{12}O_6$ in 1000 g of water ? (K_f = 1.86 K molality^{-1})

(1) –0.186° C (2) –0.372° C

(3) –0.54° C (4) –0.72° C

59. A solution of 1.25 g of a non-electrolyte in 20 g of water freezes at 271.94 K. If K_f = 1.86K molality^{-1} then the molecular wt. of the solute is :

(1) 207.8 g mol^{-1} (2) 179.79 g mol^{-1}

(3) 209.6 g mol^{-1} (4) 96.01 g mol^{-1}

60. If a thin slice of sugar beet is placed in concentrated solution of NaCl then

(1) Sugar beet will lose water from its cells

(2) Sugar beet will absorb water from solution

(3) Sugar beet will neither absorb nor lose water

(4) Sugar beet will dissolve in solution

61. In osmosis phenomenon net flow of :

(1) Solvent molecules occurs from higher concentration to lower concentration

(2) Solvent molecules occurs from lower concentration to higher concentration

(3) Solute molecules occurs from higher concentratioin to lower concentration

(4) Solute molecules occurs from lower concentration to higher concentration

62. At constant temperature the osmotic pressure of a solution is :

(1) Directly proportional to the concentration

(2) Inversely proportional to the concentration

(3) Directly proportional to the square of concentration

(4) Directly proportional to the square root of concentration

63. Which inorganic precipitate acts as semipermeable membrane ?

(1) Calcium sulphate (2) Barium oxalate

(3) Nickel phosphate (4) Copper ferrocyanide

64. 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 :
(1) There will be not net movement across the membrane
(2) Glucose will flow towards urea solution
(3) Urea will flow towards glucose solution
(4) Water will flow from urea solution towards glucose solution.

65. The best colligative property used for the determination of molecular masses of polymers is :
(1) Relative lowering in vapour pressure
(2) Osmotic pressure
(3) Elevation in boiling point
(4) Depression in freezing point

66. If mole fraction of the solvent in solution decreases then :
(1) Vapour pressure of solution increases
(2) B. P. decreases
(3) Osmotic pressure increases
(4) All are correct

67. The osmotic pressure of a solution increases if :
(1) Temperature is lowered
(2) Volume is increased
(3) Number of solute molecules is increased
(4) None

68. Which of the following solutions at the same temperature will be isotonic :
(1) 3.42 g of cane sugar in one litre water and 0.18 g of glucose in one litre water.
(2) 3.42 g of cane sugar in one litre water and 0.18 g of glucose in 0.1 litre water.
(3) 3.42 g of cane sugar in one litre water and 0.585g of NaCl in one litre water.
(4) 3.42 g of cane sugar in one litre water and 1.17 g of NaCl in one litre water.

69. If density of 2 molal sucrose solution is 1.4 g mL^{-1} at 25°C, find osmotic pressure.
(1) 4.06 atm (2) 2 atm
(3) 40.6 atm (4) 3.4 atm

70. If total concentration of dissolved particles inside red blood cells is 0.3 M (approximate) and the membrane surrounding the cell is semipermeable. Find osmotic pressure inside the cell
(1) 7.34 atm (2) 1.78 atm
(3) 2.34 atm (4) 0.74 atm

71. Equal volume of 0.1 M urea and 0.1 M glucose are mixed. The mixture will have :-
(1) Lower osmotic pressure
(2) Same osmotic pressure
(3) Higher osmotic pressure
(4) None of these

72. Osmotic pressure of a solution (density is 1g mL^{-1}) containg 3 g of glucose (molecular weight = 180) in 60 g of water at 15^0C is :
(1) 0.34 atm (2) 0.65 atm
(3) 6.25 atm (4) 5.57 atm

73. Osmotic pressure of a sugar solution at 24^0C is 2.5 atmosphere. The concentration of the solution in mole per litre is :
(1) 10.25 (2) 1.025
(3) 1025 (4) 0.1025

74. A solution containing 4 g of a non volatile organic solute per 100 ml was found to have an osmotic pressure equal to 500 cm of mercury at 27^0C. The molecular weight of solute is :
(1) 14.97 (2) 149.7 (3) 1697 (4) 1.497

75. A solution containing 8.6 g urea in one litre was found to be isotonic with 0.5% (wt./vol) solution of an organic, non volatile solute. The molecular weight of later is :
(1) 348.9 (2) 34.89 (3) 3489 (4) 861.2

76. If a 6.84% (w/V) solution of cane-sugar (mol. wt. 342) is isotonic with 1.52% (w/V) solution of thiocarbamide, then the molecular weight of thiocarbamide is :
(1) 152 (2) 76 (3) 60 (4) 180

77. A solution containing 500 g of a protein per litre is isotonic with a solution containing 3.42 g of sucrose per litre. The molecular mass of protein is
(1) 5 (2) 146
(3) 34200 (4) 50000

78. The osmotic pressure of blood is 7.65 atm. at 310 K. an aqueous solution of Glucose that will be isotonic with blood is ....w/V :
(1) 5.41% (2) 54.1%
(3) 3.5% (4) 4.53%

ABNORMAL COLLIGATIVE PROPERTIES

79. 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 :
(1) Normal (2) Associated
(3) Hydrolysed (4) Dissociated

80. van't Hoff factor is :
(1) Less than one in case of dissociation
(2) More than one in case of association
(3) Always less than one
(4) Less than one in case of association

81. The vant Hoff factor (i) for a dilute solution of $K_3[Fe(CN)_6]$ is :
(1) 10 (2) 4 (3) 5 (4) 0.25

82. The experimental molecular weight of an electrolyte will always be less than its calculated value because the value of vant Hoff factor, 'i' is :
(1) Less than 1 (2) Greater than 1
(3) One (4) Zero

83. The vant Hoff factor (i) for a dilute aqueous solution of Glucose is :
(1) Zero (2) 1.0 (3) 1.5 (4) 2.0

84. 0.585% NaCl solution at 27°C has osmotic pressure.
(1) 2.49 atm (2) 5 atm
(3) 1.2 atm (4) 3.8 atm

85 The substance A when dissolved in solvent B shows the molecular mass corresponding to A_3. The vant Hoff's factor will be -
(1) 1 (2) 2 (3) 3 (4) $\frac{1}{3}$

86. The ratio of the value of any colligative property for KCl solution to that for sugar solution is nearly .... time :
(1) 1 (2) 0.5 (3) 2 (4) 2.5

87. The lowering of vapour pressure of 0.1M aqueous solutions of NaCl, $CuSO_4$ and K_2SO_4 are :
(1) All equal
(2) In the ratio of 1 : 1 : 1.5
(3) In the ratio of 3 : 2 : 1
(4) In the ratio of 1.5 : 1 : 2.5

88. The freezing point of 1 molal NaCl solution assuming NaCl to be 100% dissociated in water is: (K_f = 1.86 K Molality^{-1})
(1) –1.86 °C (2) –3.72 °C
(3) +1.86 °C (4) + 3.72 °C

89. The molal elevation constant of water is 0.51. The boiling point of 0.1 molal aqueous NaCl solution is nearly :
(1) 100.05 °C (2) 100.1 °C
(3) 100.2° C (4) 101.0° C

90. The molal elevation constant of water is 0.52K molality^{-1}. The boiling point of 1.0 molal aqueous KCl solution (assuming complete dissociation of KCl), should be :
(1) 100.52^{0}C (2) 101.04^{0}C
(3) 99.48^{0}C (4) 98.96^{0}C

91. Solute A is ternary electrolyte and solute B is non-electrolyte. If 0.1 M solution of solute B produces an osmotic pressure of 2P, then 0.05M solution of A at the same temperature will produce an osmotic pressure equal to :
(1) P (2) 1.5 P (3) 2 P (4) 3 P

92. Phenol associates in benzene as

$$C_6H_5OH \rightleftharpoons \frac{1}{2}(C_6H_5OH)_2$$

If degree of association of phenol is 40%. van't Hoff factor i is :-
(1) 1 (2) 0.8 (3) 1.4 (4) 0.6

93. The values of observed and calculated molecular weight of calcium nitrate are respectively 65.6 and 164. The degree of dissociation of calcium nitrate will be :
(1) 25% (2) 50%
(3) 75% (4) 60%

94. A 0.004M solution of Na_2SO_4 is isotonic with a 0.010M solution of glucose at the 25°C temperature. The apparent degree of dissociation of Na_2SO_4 is
(1) 25% (2) 50%
(3) 75% (4) 85%

95. A 5.8% (wt./vol.) NaCl solution will exert an osmotic pressure closest to which one of the following :
(1) 5.8% (wt./vol) sucrose solution
(2) 5.8% (wt./vol) glucose solution
(3) 2 M sucrose solution
(4) 1 M glucose solution

96. Which salt shows maximum osmotic pressure in its 1M solution :
(1) $AgNO_3$ (2) Na_2SO_4
(3) $(NH_4)_3PO_4$ (4) $MgCl_2$

97. Which solution will exert highest osmotic pressure?
(1) 1M glucose solution (2) 1M urea solution
(3) 1M Alum solution (4) 1M NaCl solution

98. Which is the correct relation between osmotic pressure of 0.1M NaCl solution and 0.1M Na_2SO_4 solution ?
(1) The osmotic pressure of Na_2SO_4 is less than NaCl solution
(2) The osmotic pressure Na_2SO_4 is more than NaCl solution
(3) Both have same osmotic pressure
(4) None of the above

99. Which one of the following solutions will have highest osmotic pressure ? (Assume that all the salts are equally dissociated)
(1) 0.1M $Al_2(SO_4)_3$
(2) 0.1M $BaCl_2$
(3) 0.1 M Na_2SO_4
(4) The solution obtained by mixing equal volumes of (2) and (3)

100. The following solutions have equal concentrations. Which one will show minimum osmotic pressure?
(1) $BaCl_2$ (2) $AgNO_3$
(3) Na_2SO_4 (4) $(NH_4)_3PO_4$

101. The osmotic pressure of equimolor solutions of $BaCl_2$, NaCl, and glucose will be in the order :
(1) Glucose > NaCl > $BaCl_2$
(2) $BaCl_2$ > NaCl > Glucose
(3) NaCl > $BaCl_2$ > Glucose
(4) NaCl > Glucose > $BaCl_2$

102. Which one of the following pairs of solutions will be expected to be isotonic under the same temperature ?
(1) 0.1M urea and 0.1 M NaCl
(2) 0.1M urea and 0.2 M $MgCl_2$
(3) 0.1M NaCl and 0.1M Na_2SO_4
(4) 0.1M $Ca(NO_3)_2$ and 0.1M Na_2SO_4

103. Two solutions of KNO_3 and CH_3COOH are prepared separately. Molarity of both is 0.1M and osmotic pressures are P_1 and P_2 respectively. The correct relationship between the osmotic pressures is
(1) $P_2 > P_1$ (2) $P_1 = P_2$
(3) $P_1 > P_2$ (4) $\frac{P_1}{P_1+P_2} = \frac{P_2}{P_1+P_2}$

104. The correct relationship between the boiling points of very dilute solutions of $AlCl_3(T_1)$ and $CaCl_2(T_2)$, having the same molar concentration is :
(1) $T_1 = T_2$ (2) $T_1 > T_2$ (3) $T_2 = T_1$ (4) $T_2 \geq T_1$

105. Which of the following 0.1 M aqueous solutions will have the lowest freezing point :
(1) Potassium Sulphate (2) Sodium Chloride
(3) Urea (4) Glucose

106. Which aqueous solution has minimum freezing point ?
(1) 0.01 M NaCl (2) 0.005 M C_2H_5OH
(3) 0.005 M MgI_2 (4) 0.005 M $MgSO_4$

107. If α is the degree of dissociation of $K_4[Fe(CN)_6]$, then abnormal mass of complex in the solution will be :-
(1) $M_{normal} (1+2\alpha)^{-1}$ (2) $M_{normal} (1+3\alpha)^{-1}$
(3) $M_{normal} (1+\alpha)^{-1}$ (4) $M_{normal} (1+4\alpha)^{-1}$

108. Which solution will have least vapour pressure :
(1) 0.1 M $BaCl_2$ (2) 0.1 M urea
(3) 0.1 M Na_2SO_4 (4) 0.1 M Na_3PO_4

109. Which has maximum freezing point :
(1) 1 molar of NaCl solution
(2) 1 molar of KCl solution
(3) 1 molar of $CaCl_2$ solution
(4) 1 molar of urea solution

110. The freezing point of 1% aqueous solution of calcium nitrate will be :
(1) 0^0C (2) Above 0^0C
(3) 1^0C (4) Below 0^0C

111. The following aqueous solution in the correct order of decreasing freezing point is -
(1) 0.2M $BaCl_2$, 0.2M KCl, 0.1M Na_2SO_4
(2) 0.2M KCl, 0.1M Na_2SO_4, 0.2M $BaCl_2$
(3) 0.1M Na_2SO_4, 0.2M KCl, 0.2M $BaCl_2$
(4) 0.1M Na_2SO_4, 0.2M $BaCl_2$, 0.2M KCl

112. Which of the following solutions will have highest boiling point ?
(1) 1% Glucose in water (2) 1% Sucrose in water
(3) 1% NaCl in water (4) 1% Urea in water

113. The freezing point of equimolal aqueous solution will be highest for :
(1) $C_6H_5NH_3Cl$ (2) $Ca(NO_3)_2$
(3) $La(NO_3)_3$ (4) $C_6H_{12}O_6$(Glucose)

114. When mercuric Iodide is added to the aqueous solution of potassium iodide ?
(1) The boiling point does not change
(2) Freezing point is raised
(3) The freezing point is lowered
(4) Freezing point does not change

115. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to :
(1) Ionisation of benzoic acid
(2) Dimerization of benzoic acid
(3) Trimerization of benzoic acid
(4) Solvation of benzoic acid

116. 0.1 M solution of K_2SO_4 is dissolved to the extent of 90%. What would be its osmotic pressure at 27°C :-
(1) 6.89 atm (2) 0.689 atm
(3) 0.344 atm (4) 3.4 atm

117. Which one has same van't Hoff factor i as that of Hg_2Cl_2 :-
(1) NaCl (2) Na_2SO_4
(3) $Al(NO_3)_3$ (4) $Al_2(SO_4)_3$

EXERCISE-I (Conceptual Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**3**	**4**	**4**	**4**	**3**	**4**	**4**	**3**	**2**	**2**	**3**	**3**	**2**	**1**	**2**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**3**	**2**	**2**	**2**	**4**	**1**	**1**	**4**	**1**	**4**	**2**	**2**	**1**	**3**	**4**
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	**2**	**4**	**3**	**2**	**1**	**4**	**1**	**1**	**3**	**1**	**2**	**1**	**4**	**3**	**2**
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	**2**	**1**	**3**	**3**	**2**	**2**	**4**	**1**	**4**	**1**	**4**	**2**	**1**	**4**	**1**
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	**2**	**1**	**4**	**1**	**2**	**3**	**3**	**2**	**3**	**1**	**2**	**3**	**4**	**2**	**2**
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	**2**	**4**	**1**	**2**	**4**	**2**	**2**	**2**	**2**	**4**	**3**	**2**	**2**	**2**	**2**
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
Ans.	**4**	**2**	**3**	**3**	**3**	**3**	**3**	**2**	**1**	**2**	**2**	**4**	**3**	**2**	**1**
Que.	106	107	108	109	110	111	112	113	114	115	116	117			
Ans.	**1**	**4**	**4**	**4**	**4**	**3**	**3**	**4**	**2**	**2**	**1**	**2**			

EXERCISE-II (Previous Year Questions) AIPMT/NEET & AIIMS (2006-2018)

AIPMT 2006

1. A solution containing 10g per dm^3 of urea (molecular mass = 60g mol^{-1}) is isotonic with a 5% solution of a nonvolatile solute. The molecular mass of this nonvolatile solute is :
(1) 250g mol^{-1} (2) 300g mol^{-1}
(3) 350g mol^{-1} (4) 200g mol^{-1}

2. 1.00g of a non-electrolyte solute (molar mass 250g mol^{-1}) was dissolved in 51.2g of benzene. If the freezing point depression constant, K_f of benzene is 5.12 K kg mol^{-1}, the freezing point of benzene will be lowered by :
(1) 0.4 K (2) 0.3 K
(3) 0.5 K (4) 0.2 K

3. A solution of acetone in ethanol
(1) shows a positive deviation from Raoult's law
(2) behaves like a near ideal solution
(3) Obeys Raoult's law
(4) shows a negative deviation from Raoult's law

4. During osmosis, flow of water through a semipermeable membrane is :
(1) from both sides of semipermeable membrane with equal flow rates
(2) from both sides of semipermeable membrane with unequal flow rates
(3) from solution having lower concentration only
(4) from solution having higher concentration only

AIIMS 2006

5. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K and freezing point of pure water is 273·15K. The freezing point of a 5% solution (by mass) of glucose in water is –
(1) 271 K (2) 273·15 K
(3) 269·07 K (4) 277·23 K

AIPMT 2007

6.. 0.5 molal aqueous solution of a weak acid (HX) is 20% ionised. If K_f for water is1.86 K kg mol^{-1}, the lowering in freezing point of the solution is :
(1) –0.56 K (2) –1.12 K
(3) 0.56 K (4) 1.12 K

AIPMT 2009

7. A 0.0020 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 1mol of ionic compound produces on being dissolved in water will be (K_f = 1.86°C m^{-1}) :-
(1) 1 (2) 2 (3) 3 (4) 4

AIPMT 2010

8. An aqueous solution is 1.00 molal in KI. Which change will cause the vapour pressure of the solution of increase ?
(1) Addition of water
(2) Addition of NaCl
(3) Addition of Na_2SO_4
(4) Addition of 100 molal KI

9. 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})
(1) –0.570°C (2) –0.372°C
(3) –0.520°C (4) +0.372°C

AIIIMS 2010

10. For an ideal solution of A and B which statement is incorrect :-
(1) The enthalpy change of mixing of A and B is zero
(2) The volume change of solution A and B is zero
(3) The intermolecular forces of A and B is same as that of A–A and B–B
(4) The entropy change of mixture of A and B is zero

AIPMT Pre. 2011

11. The freezing point depression constant for water is –1.86°C m^{-1}. If 5 g Na_2SO_4 is dissolved in 45.0 g H_2O, the freezing point is changed by –3.82°C. Calculate the van't Hoff factor for Na_2SO_4
(1) 2.05 (2) 2.63
(3) 3.11 (4) 0.381

12. The van't Hoff factor i for a compound which undergoes dissociation in one solvent and association in other solvent is respectively :
(1) Less than one and greater than one
(2) Less than one and less than one
(3) Greater than one and less than one
(4) Greater than one and greater than one

13. Mole fraction of the solute in a 1.00 molal aqueous solution is :

(1) 0.1770 (2) 0.0177
(3) 0.0344 (4) 1.7700

AIPMT Mains 2011

14. 200 mL of an aqueous solution of a protein contain its 1.26 g. The Osmotic pressure of this solution at 300 K is found to be 2.57×10^{-3} bar. The molar mass of protein will be :-
($R = 0.083$ L bar mol^{-1} K^{-1})

(1) 61038 g mol^{-1} (2) 51022 g mol^{-1}
(3) 122044 g mol^{-1} (4) 31011 g mol^{-1}

AIPMT Pre 2012

15. p_A and p_B are the vapour pressure of pure liquid components, A and B, respectively of an ideal binary solution. If x_A represents the mole fraction of component A, the total pressure of the solution will be.

(1) $p_B + x_A (p_B - p_A)$ (2) $p_B + x_A (p_A - p_B)$
(3) $p_A + x_A (p_B - p_A)$ (4) $p_A + x_A (p_A - p_B)$

AIPMT Mains 2012

16. Which of the following compounds can be used as antifreeze in automobile radiators ?

(1) Nitrophenol (2) Ethyl alcohol
(3) Methyl alcohol (4) Glycol

17. Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 25°C are 200 mmHg and 415 mmHg respectively. Vapour pressure of the solution obtained by mixing 25.5 g of $CHCl_3$ and 40g of CH_2Cl_2 at the same temperature will be: (Molecular mass of $CHCl_3$ = 119.5 u and molecular mass of CH_2Cl_2 = 85 u)

(1) 347.9 mmHg (2) 280.5 mmHg
(3) 173.9 mmHg (4) 615 mmHg

NEET-UG 2013

18. 6.02×10^{20} molecules of urea are present in 100mL of its solution. The concentration of solution is :-

(1) 0.1 M (2) 0.02 M
(3) 0.01 M (4) 0.001M

AIIMS 2013

19. Boiling point of benzene is 353.23 K. When 1.8 g of non-volalite solute is dissolved in 90 g of benzene. Then boiling point raised to 354.11 K. Given K_b (benzene) = 2.53Kkgmol^{-1}. Then molecular mass of non volatile substance is :-

(1) 58g mol^{-1} (2) 120 g mol^{-1}
(3) 116 g mol^{-1} (4) 60 g mol^{-1}

20. Strength of H_2O_2 is 15.18 g L^{-1}, then it is equal to:-

(1) 1 volume (2) 10 volume
(3) 5 volume (4) 7 volume

AIPMT 2014

21. Of the following 0.10m aqueous solutions, which one will exhibit the largest freezing point depression?

(1) KCl (2) $C_6H_{12}O_6$
(3) $Al_2(SO_4)_3$ (4) K_2SO_4

AIIMS 2014

22. Addition of 1 kg of non volatile solute in volatile solvent increases the boiling point from 350 K to 355 K and decreases the freezing point from 250 K to 220 K. If K_b is 15.5 K Kg mol^{-1}, then K_f will be

(1) 2.1 Kkgmol^{-1} (2) 93.0 Kkgmol^{-1}
(3) 76 Kkgmol^{-1} (4) 10 Kkgmol^{-1}

AIPMT 2015

23. The boiling point of 0.2 mol kg^{-1} solution of X in water is greater than equimolal solution of Y in water. Which one of the following statements is **true** in this case ?

(1) Molecular mass of X is greater than the molecular mass of Y.
(2) Molecular mass of X is less than the molecular mass of Y.
(3) Y is undergoing dissociation in water while X undergoes no change.
(4) X is undergoing dissociation in water while Y undergoes no change.

24. Which one is **not** equal to zero for an ideal solution:-

(1) ΔS_{mix}
(2) ΔV_{mix}
(3) $\Delta P = P_{observed} - P_{Raoult}$
(4) ΔH_{mix}

25. Which one of the following electrolytes has the same value of van't Hoff's factor (i) as that of the $Al_2(SO_4)_3$ (if all are 100% ionised) ?

(1) $K_3[Fe(CN)_6]$

(2) $Al(NO_3)_3$

(3) $K_4[Fe(CN)_6]$

(4) K_2SO_4

Re-AIPMT 2015

26. What is the mole fraction of the solute in a 1.00 m aqueous solution ?

(1) 0.0354
(2) 0.0177
(3) 0.177
(4) 1.770

AIIMS 2015

27. Osmotic pressure of a solution containing 1 g protein in 100 mL solution at 300 K is 1.66 bar. What is the molecular weight of protein

($R = 0.083\ L\ bar\ mol^{-1}\ K^{-1}$)

(1) 150
(2) 120
(3) 130
(4) 300

28. On adding a non volatile solute to a solvent, the vapour pressure of solvent decreases and becomes z × [vapour pressure of solvent) where z is

(1) mole fraction of solvent

(2) mole fraction of solute

(3) molality

(4) molarity

NEET-I 2016

29. Which of the following statement about the composition of the vapour over an ideal a 1 : 1 molar mixture of benzene and toluene is **correct**? Assume that the temperature is constant at (25°C). (Given : Vapour Pressure Data at 25°C, benzene = 12.8 kPa, Toluene = 3.85 kPa)

(1) The vapour will contain a higher percentage of benzene

(2) The vapour will contain a higher percentage of toluene

(3) The vapour will contain equal amounts of benezene and toluene

(4) Not enough information is given to make a predication

30. At 100°C the vapour pressure of a solution of 6.5g of a solute in 100 g water is 732 mm. If $K_b = 0.52\ °C\ m^{-1}$, the boiling point of this solution will be :-

(1) 101°C
(2) 100°C
(3) 102°C
(4) 103°C

31. Consider the following liquid - vapour equilibrium.

Liquid $\rightleftharpoons$ Vapour

Which of the following relations is **correct** ?

(1) $\dfrac{d\ell nG}{dT^2} = \dfrac{\Delta H_v}{RT^2}$

(2) $\dfrac{d\ell nP}{dT} = \dfrac{-\Delta H_v}{RT}$

(3) $\dfrac{d\ell nP}{dT^2} = \dfrac{-\Delta H_v}{T^2}$

(4) $\dfrac{d\ell nP}{dT} = \dfrac{\Delta H_v}{RT^2}$

NEET-II 2016

32. The van't Hoff factor (i) for a dilute aqueous solution of the strong electrolyte barium hydroxide is

(1) 2
(2) 3
(3) 0
(4) 1

33. Which one of the following is **incorrect** for ideal solution ?

(1) $\Delta P = P_{obs} - P_{\text{calculated by Raoult's law}} = 0$

(2) $\Delta G_{mix} = 0$

(3) $\Delta H_{mix} = 0$

(4) $\Delta U_{mix} = 0$

AIIMS 2016

34. 0.5 mol NaCl is dissolved in 500g H_2O. Then determine freezing point and boilling point of solution.

Given $(K_f)_{H_2O} = 1.8\ K\ kg\ mol^{-1}$,

$(K_b)_{H_2O} = 0.5\ K\ kg\ mol^{-1}$

(1) –1.8 °C, 100.5 °C

(2) –3.6 °C, 101 °C

(3) –3.6 °C, 99 °C

(4) 0 °C, 100 °C

35. 1g solute is dissolved in 50 g benzene shows depression in freezing point by 0.4 K. Then calculate molar mass of solute if $K_f = 5.12\ K\ kg\ mol^{-1}$

(1) 512
(2) 256
(3) 728
(4) 738

36. If the density of methanol is 0.8 kgL^{-1}, what is the volume needed for making 2.5 L of its 0.4 M solution ?

(1) 0.4 L
(2) 4.0 L
(3) 0.04 L
(4) 40 L

37. When nonvolatile solute is added in a solvent then relative lowering in vapour pressure depends upon:-

(1) $\frac{\text{Number of moles of solute}}{\text{Number of moles of solvent}}$

(2) $\frac{\text{Number of moles of solvent}}{\text{Number of moles of solute}}$

(3) $\frac{\text{Number of moles of solvent}}{\text{Total number of moles of solution}}$

(4) $\frac{\text{Number of moles of solution}}{\text{Number of moles of solute}}$

NEET(UG) 2017

38. If molality of a dilute solution is doubled, the value of molal depression constant (K_f) will be :-

(1) halved (2) tripled
(3) unchanged (4) doubled

39. Which of the following is dependent on temperature?

(1) Molarity (2) Mole fraction
(3) Weight percentage (4) Molality

AIIMS 2017

40. 5g of an unknown solute is dissolved in 295 g solvent. If molarity and density of solution are 0.05 M and 1.5 g cc^{-1} respectively. The molecular weight of unknown solute is :-

(1) 375 (2) 425 (3) 400 (4) 500

41. The depression in freezing point of water containing ethylene glycol is 7.4°C. Calculate the mass of ethylene glycol added in 500 g water.

(K_f = 1.86 K kg mol^{-1}).

(1) 23.3 g (2) 233.3 g
(3) 123.3 g (4) 12.33 g

42. The molality of a solution containing 3g CH_3COOH in 50 g benzene is :-

(1) 0.1 m (2) 0.5 m
(3) 0.2 m (4) 1 m

AIIMS 2018

43. 45 g non volatile solute A is dissolved in 600 g of water if depression in freezing point is 2.2 K. Then what will be molar mass of solute :-

(1) 126.8 (2) 31.7 (3) 63.4 (4) 158.5

44. 1 g of a protein polymer having molar mass 16×10^4 is present in 800 mL solution at 300K then osmotic pressure (in pascal) is
[R = 8.314 J mol^{-1} K^{-1}]:-

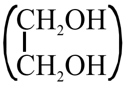
(1) 0.4 (2) 0.02 (3) 0.04 (4) 0.2

45. For 1% H_2SO_4 solution find it's normality (approx)

(1) 0.1 (2) 0.2 (3) 0.4 (4) 0.02

46. 0.04 molal aqueous monoprotic acid has depression in freezing point equal to 0.1 K then find vant Hoff factor for acid :-

(1) 1 (2) 2 (3) 2.5 (4) 1.34

47. Ethylene glycol 
$\left(\begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}\right)$
is used as an antifreezing agent. Mass of enthylene glycol which should be added to 2 litre of water to present it from freezing at –24°C will be

(K_f for water = 1.86 K kg mol^{-1})

(1) 1600 g (2) 1200 g
(3) 800 g (4) 400 g

EXERCISE-II (Previous Year Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**2**	**1**	**1**	**2**	**3**	**4**	**2**	**1**	**2**	**4**	**2**	**3**	**2**	**1**	**2**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**4**	**1**	**3**	**1**	**3**	**3**	**2**	**4**	**1**	**3**	**2**	**1**	**1**	**1**	**1**
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	**4**	**2**	**2**	**2**	**2**	**3**	**1**	**3**	**1**	**4**	**3**	**4**	**3**	**4**	**2**
Que.	46	47													
Ans.	**4**	**1**													

EXERCISE-III (Analytical Questions)

Check Your Understanding

1. Which of the following solutions has the highest normality :-
(1) 8 g of KOH per litre
(2) 1 N phosphoric acid
(3) 6 g of NaOH per 100 mL
(4) 0.5 M H_2SO_4

2. An aqueous solution of glucose is 10% in strength. The volume in which 2 g mole of it is dissolved will be :-
(1) 18 litre (2) 3.6 litre
(3) 0.9 litre (4) 1.8 litre

3. One litre of N/2 HCl solution is heated in a beaker. It was observed that when the volume of the solution was reduce to 600 mL, 3.25 g of HCl in lost, calculate the normality of the new solution
(1) 1.70 (2) 0.685
(3) 0.342 (4) 0.171

4. The mole fraction of the solute in one molal aqueous solution is :-
(1) 0.027 (2) 0.036
(3) 0.018 (4) 0.009

5. Density of a 2.05 M solution of acetic acid in water is 1.02 g mL^{-1}. The molality of the solution is :
(1) 1.14 mol kg^{-1} (2) 3.28 mol kg^{-1}
(3) 2.28 mol kg^{-1} (4) 0.44 mol kg^{-1}

6. What will be density (in g mL^{-1}) of 3.60 molar sulphuric acid having 29% by mass.
(Molar mass = 98 g mol^{-1})
(1) 1.88 (2) 1.22
(3) 1.45 (4) 1.64

7. The molality of a urea solution in which 0.0100g of urea. [$(NH_2)_2CO$] is added to 0.3000 dm^3 of water at STP is :-
(1) 0.555 m (2) 5.55×10^{-4} m
(3) 33.3 m (4) 3.33×10^{-2} m

8. The concentration of a solution of H_2O_2 is 6.8%(w/V) then the volume concentration of the solution is:-
(1) 22.4 (2) 11.2
(3) 20 (4) 5

9. A gaseous mixture was prepared by taking equal mole of CO and N_2. If the total pressure of the mixture was found 1 atmosphere, the partial pressure of the nitrogen (N_2) in the mixture is :
(1) 0.5 atm (2) 0.8 atm
(3) 0.9 atm (4) 1 atm

10. The vapour pressure of two liquids 'P' and 'Q' are 80 and 60 torr, respectively. The total vapour pressure of solution obtained by mixing 3 mole of P and 2 mol of Q would be :-
(1) 68 torr (2) 140 torr
(3) 72 torr (4) 20 torr

11. Which of the following plots does not represent the behaviour of an ideal binary liquid solution :-
(1) Plot of P_A versus X_A (mole fraction of A in liquid phase) is linear
(2) Plot of P_B versus X_B is linear
(3) Plot of p_{total} versus X_A (or X_B) is linear
(4) Plot of p_{total} versus X_A is non linear

12. The vapour pressure of two pure liquids (A) and (B) are 100 and 80 torr respectively. The total pressure of the solution obtained by mixing 2 mol of (A) and 3 mol of (B) would be
(1) 20 torr (2) 36 torr
(3) 88 torr (4) 180 torr

13. For a solution of two liquids A and B, it was proved that $P = X_A (P_A^0 - P_B^0) + P_B^0$. The solution is:–
(1) Ideal
(2) Non ideal
(3) Both (1) and (2)
(4) None of the above

14. Mole fraction of A vapours above solution in mixture of A and B ($X_A = 0.4$) will be :-
(P_A° = 100mm, P_B° = 200mm)
(1) 0.4 (2) 0.8
(3) 0.25 (4) None

15. The vapour pressure of pure benzene and toluene are 160 and 60 torr respectively. The mole fraction of toluene in vapour phase in contact with equimolar solution of benzene and toluene is:
(1) 0.50 (2) 0.6
(3) 0.27 (4) 0.73

16. The vapour pressure of ethanol and methanol are 42.0 mm and 88.5 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 46.0 g of ethanol with 16.0 g of methanol. The mole fraction of methanol in the vapour is :
(1) 0.467 (2) 0.502
(3) 0.513 (4) 0.556

17. A solution has a 1 : 4 mole ratio of pentane to hexane. The vapour pressures of the pure hydrocarbons at 20°C are 440 mm Hg for pentane and 120 mm Hg for hexane. The mole fraction of pentane in the vapour phase would be :-

(1) 0.200 (2) 0.478

(3) 0.549 (4) 0.786

18. 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 presure (in mm) at the same temperature will be

(1) 300 (2) 700

(3) 360 (4) 350

19. A mixture of liquid showing positive deviation in Raoult's law is :-

(1) $(CH_3)_2$ CO + C_2H_5OH

(2) $(CH_3)_2CO$ + $CHCl_3$

(3) $(C_2H_5)_2O$ + $CHCl_3$

(4) $(CH_3)_2CO$ + $C_6H_5NH_2$

20. An ideal solution was obtained by mixing methanol and ethanol. If the partial vapour pressure of methanol and ethanol are 2.619 K Pa and 4.556 K Pa respectively, the composition of vapour (in terms of mole fraction) will be -

(1) 0.635 MeOH, 0.365 EtOH

(2) 0.365 MeOH, 0.635 EtOH

(3) 0.574 MeOH, 0.326 EtOH

(4) 0.173 MeOH, 0.827 EtOH

21. Azeotropic mixture are :

(1) Mixture of two solids

(2) Those which boil at different temperatures

(3) Those which can be fractionally distilled

(4) Constant boiling mixtures

22. An azeotropic mixture of two liquids boil at a lower temperature than either of them when

(1) It is saturated

(2) It does not deviate from Raoult's law

(3) It shows negative deviation from Raoult's law

(4) It shows positive deviation from Raoult's law

23. The azeotropic mixture of water (B.P 100.15°C) and HCl (B.P. –85°C) boils at 108.5°C. When this mixture is distilled, it is possible to obtain :

(1) Pure HCl

(2) Pure water

(3) Pure water as well as HCl

(4) Neither HCl nor H_2O in their pure states

24. Colligative properties depend on the :-

(1) Relative no. of solute molecules in solution and the nature of the solvent

(2) Relative no. of solute molecules in solvent and the nature of solute

(3) Relative no. of solute molecules and the nature of solute and solvent

(4) Relative no. of solute molecules, irrespective of the nature of solvent and solute

25. The vapour pressure of a solvent decreases by 10 mm. of Hg 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 vapour pressure is to be 20 mm of Hg :-

(1) 0.2 (2) 0.4 (3) 0.6 (4) 0.8

26. The vapour pressure of a solution of 5 g. of non electrolyte in 100 g. of water at a particular temperature is 2985 Nm^{-2}. The vapour pressure of pure water at that temperature is 3000 Nm^{-2}. The molecular weight of the solute is :-

(1) 180 (2) 90

(3) 270 (4) 200

27. How many gram of a non volatile solute having a molecular weight of 90 are to be dissolved in 97.5 g water in order to decrease the vapour pressure of water by 2.5 percent :-

(1) 25 (2) 18

(3) 12.5 (4) 9

28. The vapour pressure of a pure liquid solvent (X) is decreased to 0.60 atm. from 0.80 atm on addition of a non volatile substance (Y). The mole fraction of (Y) in the solution is:-

(1) 0.20 (2) 0.25

(3) 0.5 (4) 0.75

29. 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of this aqueous solution at 100 °C is :

(1) 759.00 torr (2) 7.60 torr

(3) 76.00 torr (4) 752.40 torr

30. Water is added to the solution such that the mole fraction of water in the solution becomes 0.9. The boiling point of the solution is

(1) 354.7 K (2) 375.5 K

(3) 376.2 K (4) 380.4 K

31. Glucose is added to 1 litre water to such an extent that $\frac{\Delta T_f}{K_f}$ becomes equal to $\frac{1}{1000}$, the wt. of glucose added is :-

(1) 180 g
(2) 18 g
(3) 1.8 g
(4) 0.18 g

32. A solution of urea boils at 100.18°C at the atomospheric pressure. If K_f and K_b for water are 1.86 and 0.512K kg mol^{-1} respectively, the above solution will freeze at :-

(1) –6.54°C
(2) –0.654°C
(3) 6.54°C
(4) 0.654°C

33. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at – 6°C will be : (K_f for water = 1.86 K $kgmol^{-1}$, and molar mass of ethylene glycol = 62 $gmol^{-1}$)

(1) 400.00 g
(2) 304.60 g
(3) 800.00 g
(4) 204.30 g

34. K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to –2.8°C ?

(1) 27 g
(2) 72 g
(3) 93 g
(4) 39 g

35. Osmosis of A into solution B will not take place if:-

(1) A is hypertonic
(2) A is hypotonic
(3) A is isotonic
(4) Either 1 or 3 may correct

36. Insulin $(C_2H_{10}O_5)_n$ is dissolved in a suitable solvent and the osmotic pressure (π) of solutions of various concentrations (g cm^{-3}) C is measured at 20 °C. The slope of a plot of π against C is found to be 4.65×10^{-3}. The molecular weight of the insulin is

(1) 4.8×10^5
(2) 9×10^5
(3) 3×10^5
(4) 5.16×10^6

37. 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 the blood stream

(1) 0.16 mol L^{-1}
(2) 0.32 mol L^{-1}
(3) 0.60 mol L^{-1}
(4) 0.45 mol L^{-1}

38. Camphor is often used in molecular mass determination because :-

(1) It has a very high cryoscopic constant
(2) It is volatile
(3) It is solvent for organic substances
(4) It is readily available

39. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass=60g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 gcm^{-3}, molar mass of the substance will be.

(1) 115.0 g mol^{-1}
(2) 105.0 g mol^{-1}
(3) 210.0 g mol^{-1}
(4) 90.0 g mol^{-1}

40. A 5% solution of cane sugar (molar mass 342) is isotonic with 1% of a solution of an unknown solute. The molar mass of unknown solute in g mol^{-1} is :-

(1) 136.2
(2) 171.2
(3) 68.4
(4) 34.2

41. The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression :-

(1) $\alpha = \frac{x+y-1}{i-1}$
(2) $\alpha = \frac{x+y+1}{i-1}$
(3) $\alpha = \frac{i-1}{(x+y-1)}$
(4) $\alpha = \frac{i-1}{x+y+1}$

42. The van't Hoff factor for 0.1 M $Ba(NO_3)_2$ solution is 2.74 . The degree of dissociation is :-

(1) 91.3%
(2) 87%
(3) 100%
(4) 74%

43. Arrange the following aqueous solutions in the order of their increasing boiling points :-

(i) 10^{-4} M NaCl
(ii) 10^{-4} M Urea
(iii) 10^{-3} M $MgCl_2$
(iv) 10^{-2} M NaCl

(1) (i) < (ii) < (iv) < (iii)
(2) (ii)<(i)=(iii)<(iv)
(3) (ii)<(i)<(iii)<(iv)
(4) (iv)<(iii)<(i)=(ii)

44. The relationship between the values of osmotic pressure of solutions obtained by dissolving 6.00 gL^{-1} of CH_3COOH (π_1) and 7.45 gL^{-1} of KCl (π_2) is :-

(1) $\pi_1 > \pi_2$
(2) $\pi_1 < \pi_2$
(3) $\pi_1 = \pi_2$
(4) None of these

45. Among 0.1M solutions of urea, Na_3PO_4 and $Al_2(SO_4)_3$:-

(a) The vapour pressure and freezing point are the lowest for urea

(b) The vapour pressure and freezing point are the highest for urea

(c) The elevation in boiling point is the highest for $Al_2(SO_4)_3$

(d) The depression in freezing point is the highest for $Al_2(SO_4)_3$

(1) Only a (2) b & c both
(3) b, c and d (4) a, b, c and d

46. When equimolar aqueous solutions of glucose, sodium chloride and barium nitrate are compared the vapour pressure of the solutions will be in the following order :-

(1) Glucose > NaCl > $Ba(NO_3)_2$
(2) Glucose = NaCl = $Ba(NO_3)_2$
(3) $Ba(NO_3)_2$ > NaCl > Glucose
(4) NaCl > $Ba(NO_3)_2$ > Glucose

47. What is the freezing point of a solution containing 8.1 g of HBr in 100g water assuming the acid to be 90% ionised (K_f for water = 1.86 K molality^{-1})

(1) 0.85°C (2) –3.53°C
(3) 0°C (4) –0.35°C

48. A 0.2 molal aqueous solution of a weak acid (HX) is 20% ionised. The elevation in boiling point of this solution is (given K_b = 0.52°C kg mol^{-1} for H_2O)

(1) 0.81 (2) 0.125
(3) 0.48 (4) 1.3

49. The substance when dissolved in water would decrease the vapour pressure of water to the greatest extent is :-

(1) 0.1 M KCl (2) 0.1 M urea
(3) 0.1 M $BaCl_2$ (4) 0.1 M NaCl

50. The molar mass of NaCl determined by the osmotic pressure method will be :–

(1) Higher than the theoretical value
(2) Lower than the theoretical value
(3) The same as the theoretical value
(4) None of these

51. Consider separate solution of 0.500 M C_2H_5OH(aq), 0.100 M $Mg_3(PO_4)_2$(aq), 0.250 M KBr(aq) and 0.125 M Na_3PO_4(aq) at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes ?

(1) 0.125 M Na_3PO_4 (aq) has the highest osmotic pressure.
(2) 0.500 M C_2H_5OH (aq) has the highest osmotic pressure.
(3) They all have the same osmotic pressure.
(4) 0.100 M $Mg_3(PO_4)_2$ (aq) has the highest osmotic pressure.

EXERCISE-III (Analytical Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**3**	**2**	**2**	**3**	**3**	**2**	**2**	**1**	**1**	**3**	**4**	**3**	**1**	**3**	**3**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**3**	**2**	**4**	**1**	**2**	**4**	**4**	**4**	**1**	**3**	**1**	**3**	**2**	**4**	**3**
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	**4**	**2**	**3**	**3**	**4**	**4**	**1**	**1**	**3**	**3**	**3**	**2**	**3**	**2**	**3**
Que.	46	47	48	49	50	51									
Ans.	**1**	**2**	**2**	**3**	**2**	**3**									

EXERCISE-IV (Assertion & Reason) Target AIIMS

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.

(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.

(C) If Assertion is True but the Reason is False.

(D) If both Assertion & Reason are false.

1. ***Assertion :–*** The molality of the solution doesn't change with change in temperature.
Reason :– The molality is expressed in units of moles per 1000 mL solution.
(1) A (2) B (3) C (4) D

2. ***Assertion :–*** The sum of the mole fraction of all the components is unity.
Reason :– Mole fraction is a temperature dependent mode of concentraction.
(1) A (2) B (3) C (4) D

3. ***Assertion :–*** A solution which contains one gram equivalent of solute per litre of the solution is called normal solution.
Reason :– A normal solution mean a solutions in which the solute doesn't associate or dissociate.
(1) A (2) B (3) C (4) D

4. ***Assertion :–*** The molarity and normality of a solution of sodium carbonate are same.
Reason :– Normality is the product of molarity & valency factor.
(1) A (2) B (3) C (4) D

5. ***Assertion :–*** Ideal solutions are one which obeys Raoult's law at all temperature and concentration.
Reason :– Very dilute solution can be treated as ideal solution.
(1) A (2) B (3) C (4) D

6. ***Assertion :–*** Cooking time is reduced in pressure cookers.
Reason :– Boiling point inside the pressure cooker is raised.
(1) A (2) B (3) C (4) D

7. ***Assertion :–*** In positive deviation of non-ideal solution attraction between solute solvent is less than the attraction between solute-solute and solvent-solvent.
Reason :– In negative deviation of non-ideal solution attraction between solute-solvent is more than the attraction between solute-solute and solvent-solvent.
(1) A (2) B (3) C (4) D

8. ***Assertion :–*** Isotonic solutions don't show net phenomenon of osmosis.
Reason :– Isotonic solutions have equal osmotic pressure at constant temp.
(1) A (2) B (3) C (4) D

9. ***Assertion :–*** When Benzoic acid is dissolved in benzene its vant Hoff factor is less than one.
Reason :– In benzene, benzoic acid has tendency to form dimer.
(1) A (2) B (3) C (4) D

10. ***Assertion :–*** Non-ideal solutions form azeotropic mixture.
Reason :– Boiling point of azeotropic mixture is only higher than boiling points of both the components.
(1) A (2) B (3) C (4) D

11. ***Assertion :–*** van't Hoff factor for benzoic acid in benzene is one.
Reason :– Benzoic acid behaves as a weaker electrolyte in benzene.
(1) A (2) B (3) C (4) D

12. ***Assertion :–*** van't Hoff factor is always more or equal to one.
Reason :– van't Hoff factor is the ratio of experimental colligative properties to observed colligative properties.
(1) A (2) B (3) C (4) D

13. ***Assertion :–*** Azeotropic mixture can't be separated by fractional distillation.
Reason :– Azeotropic mixtures are constant boiling mixtures.
(1) A (2) B (3) C (4) D

14. ***Assertion :–*** $\Delta H_{mix.}$ and $\Delta V_{mix.}$ for the preparation of ideal solution is zero.
Reason :– A-B interaction in ideal solution are same as between A-A and B-B in the two liquids before mixing.
(1) A (2) B (3) C (4) D

15. ***Assertion :–*** 0.1M solution of NaCl have low freezing point than 0.1M urea solution.
Reason :– Van't Hoff factor (No. of particles) for NaCl is more than urea.
(1) A (2) B (3) C (4) D

16. ***Assertion :-*** A non volatile solute is mixed in a solution then elevation in boiling point and depression in freezing point both are 2K.
Reason :- Elevation in boiling point and depression in freezing point both depend on melting point of non-volatile solute
(1) A (2) B (3) C (4) D

17. ***Assertion :*** Elevation in boiling point of 0.1 M KCl and 0.1 M $CaCl_2$ is same.
Reason : Because colligative properties depends on molarity only.
(1) A (2) B (3) C (4) D

18. ***Assertion :-*** On mixing aniline and Acetone shows +ve deviation.
Reason :- Interaction between Acetone and aniline is weaker than interaction of Acetone-Acetone and aniline-aniline.
(1) A (2) B (3) C (4) D

19. ***Assertion :-*** When two volatile liquids are mixed then vapour pressure of one increases and other decreases.
Reason :- Vapour pressure of solution decreases.
(1) A (2) B (3) C (4) D

20. ***Assertion :-*** At high altitude cooking food is difficult.
Reason :- Water boils at high temprature.
(1) A (2) B (3) C (4) D

21. ***Assertion :-*** After adding non-volatile solute freezing point of solvent depressed.
Reason :- Vapour pressure of solvent decreases and become equal to solid solvent, at temprature lower than the freezing point of pure solvent.
(1) A (2) B (3) C (4) D

22. ***Assertion :*** On increasing pressure solubility of gases in liquid solvent increases.
Reason : Dissolution of gases in liquid is exothermic.
(1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**3**	**3**	**3**	**4**	**2**	**1**	**2**	**1**	**1**	**3**	**4**	**4**	**1**	**1**	**1**
Que.	16	17	18	19	20	21	22								
Ans.	**4**	**4**	**4**	**4**	**3**	**1**	**2**								

IMPORTANT NOTES