02

Solutions

IN THIS CHAPTER ....

Solution is a homogeneous mixture of two or more substances. A solution of two substances is called a **binary solution.** The substances forming the solution are called **components** of the solutions. As a generalisation, the component present in smaller amount is called **solute** and the other present in larger amount is called **solvent**.

Types of Solutions

In case of binary solutions, each component may be solid, liquid or in gaseous state and on this basis different types of solutions are possible as summarised, in the following table.

Different Types of Solutions

Types of solution	Solute	Solvent	Common example
Gaseous solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

Remember A solution in which water is the solvent is called an **aqueous solution.** The solutions in which solid is present in larger proportion are called **solid solutions**. **Amalgam** is a solution of liquid in solid. **Alloys** are solution of a solid is another solid.

Solubility

The maximum amount of a solute that can be dissolved in a given amount of solvent (generally 100 g) at a given temperature is termed as **solubility** at that temperature.

Solubility of Gas in Liquid

All gases are soluble in water as well as in other liquids to a greater or lesser extent. The solubility of a gas in liquids depends upon the following factors

1. Nature of the Gas

The gases which can be easily liquified, are more soluble in common solvents, e.g. CO_2 is more soluble than H_2 and O_2 in water. Different gases dissolve to a different extent in the same solvent and same gas has different solubilities in different solvents.

e.g. non-polar gases like O_2, N_2 etc., are very less soluble in water whereas polar gases like HCl, SO_2, NH_3, CO_2 etc., are highly soluble in water.

2. Nature of the Solvent

The gases which are capable of forming ions in aqueous solutions are much more soluble in water than in other solvents. e.g. gases like HCl and NH_3 are highly soluble in water but not in organic solvents in which these do not ionise.

3. Temperature

The solubility of most gases in liquids decreases with increase of temperature. When a solution of a gas is heated, the gas is usually expelled.

However, some gases are more soluble at higher temperature than at lower. e.g. H_2 and inert gases are slightly more soluble in non-aqueous slovents with increase in temperature.

4. Pressure

The solubility of a gas in liquid is also influenced by pressure. The relation between the solubility and pressure is given by **Henry's law.** According to this law,

$$p \propto \chi \; ; \; p = K_H \chi, \; m \propto p \quad \text{or} \quad m = K_H p \qquad \ldots\text{(i)}$$

where, m = mass of the gas dissolved per unit volume of a solvent

χ = mole fraction of gas in liquid

p = pressure of the gas at equilibrium with the solution

K_H = Henry's constant

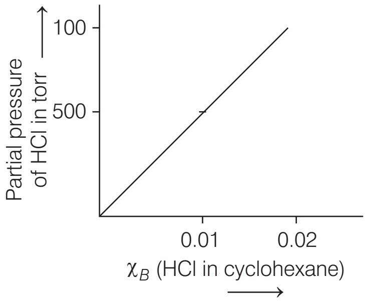
Thus, Henry's law can also be stated as, the pressure of a gas over a solution in which the gas is dissolved is equal to the amount fraction of the dissolved gas multiplied by Henry's constant. Also in other words Henry's law states that mass of a gas dissolved per unit volume of the solvent at constant temperature is directly proportional to the pressure of gas.

Different gases have different K_H values at the same temperature. This suggests that K_H is a function of the nature of the gas. Table gives K_H values of some common gases at specified temperature.

Values of Henry's law Constant (K_H) for Some Selected Gases in Water

Gas	Temp. (K)	K_H (k bar)	Gas	Temp. (K)	K_H (kbar)
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	HCHO	298	1.83×10^{-5}
N_2	303	88.84	CH_4	298	0.413
O_2	293	34.86	Vinyl chloride	298	0.611
O_2	303	46.82	($CH_2{=}CH{-}Cl$)		

It is obvious from Eq. (i) that higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid. It can be seen from Table that the K_H value for both N_2 and O_2 increases with increase of temperature indicating that the solubility of gases decreases with increase of temperature. It is due to this reason that aquatic species are more comfortable in cold water rather than in warm water.



Plot of solubility of HCl gas in cyclohexane at 293 K.

Limitations of Henry's Law

- At high pressures, the law becomes less accurate and the proportionality constant shows considerable deviations.
- Also Henry's law will hold true if temperature is not too low.
- Henry's law is only applicable when gas is not highly soluble (i.e. not under high pressure) and also when gas neither react chemically with the solvent nor dissociate or associate with the solvent.

Applications of Henry's Law

- **Production of carbonated beverages** Soft drinks, soda water and other carbonated beverages contains dissolved carbon dioxide. In the preparation of these beverages, CO_2 is passed at high pressure to increase its solubility.
- **Functioning of lungs** In lungs, oxygen present in the inhaled air dissolves in blood because of its high partial pressure and combines with haemoglobin to form oxyhaemoglobin. In tissues, where partial pressure of oxygen is low, oxyhaemoglobin releases oxygen for its utilisation in cellular activities.

- **Anoxia in climbers** At higher altitudes, the partial pressure of oxygen is less than that at the ground level. This leads to low concentration of oxygen in blood and other tissues of the people living at higher altitudes or those of mountain climbers. The low content of blood oxygen causes the climbers to become weak and reduces their thinking ability which are symptoms of conditions called *anoxia*.
- **Deep sea diving** Scuba divers (deep sea divers carrying breathing kit containing compressed air) suffer from the painful effects called *bends* when they come towards the surface.

  These painful effects arise due to decompression of gases dissolved in their blood while breathing air at high pressure under water.

  These bends are minimised by using compressed air that has been diluted with less soluble helium in the breathing apparatus. In general, a compresed gaseous mixture of 11.7% He, 56.2% N_2 and 32.1% O_2 is used in breathing kit (called scuba).

Example 1. H_2S, *a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of* H_2S *in water at STP is* 0.195 m , *calculate Henry's law constant.* ***(NCERT)***

(a) 152 bar (b) 100 bar (c) 200 bar (d) 282 bar

Sol. (*d*) Since, molality is given and molality is the moles present in 1000 g of water so first we find the moles of H_2S.
Using the formula,

$$\chi_{H_2S} = \frac{n_{H_2S}}{n_{H_2S} + n_{H_2O}}$$

calculate Henry's law constant.

Calculation of mole fraction of H_2S 0.195 m means that 0.195 mole of H_2S are dissolved in 1000 g of water.

Number of moles of water in 1000 g, (n_{H_2O})

$$= \frac{(1000\text{ g})}{(18\text{ g mol}^{-1})} = 55.55\text{ mol}$$

$$\text{Mole fraction } H_2S\ (\chi_{H_2S}) = \frac{n_{H_2S}}{n_{H_2S} + n_{H_2O}}$$

$$= \frac{(0.195\text{ mol})}{(0.195 + 55.55)\text{ mol}}$$

$$= \frac{(0.195\text{ mol})}{(55.745\text{ mol})} = 0.0035$$

Calculation of Henry's law constant

According to Henry's law,

$$\chi_{H_2S} = \frac{\text{partial pressure of } H_2S}{K_H \text{ for } H_2S} \text{ at STP}$$

$$K_H \text{ for } H_2S = \frac{\text{partial pressure of } H_2S}{\chi_{H_2S}}$$

$$= \frac{(0.987\text{ bar})}{(0.0035)} = 282\text{ bar}$$

Example 2. *Which one of the following statements regarding Henry's law is not correct?* ***(JEE Main 2019)***

(a) Different gases have different K_H (Henry's law constant) values at the same temperature
(b) Higher the value of K_H at a given pressure, higher is the solubility of the gas in the liquids
(c) The value of K_H increases with increase of temperature and K_H is function of the nature of the gas
(d) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution

Sol. (*b*) At constant temperature, solubility of a gas (S) varies inversely with Henry's law constant (K_H)

$$K_H = \frac{\text{Pressure}}{\text{Solubility of a gas in a liquid}} = \frac{p}{S}$$

Thus, higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

Solubility of Liquid in Liquid

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

(i) **Miscible** When two substances dissolve in each other, these are said to be completely miscible, e.g. water and alcohol, benzene and toluene.
(ii) **Immiscible** Two chemically different liquids such as water and oil, water and mercury, do not dissolve in each other and are said to be completely immiscible.
(iii) **Partially miscible** Certain liquids like water and phenol, water and ether, which dissolve only to a limited extent are known as partially miscible.

Solubility of Solid in Liquid

Solubility of solid solutes increases or decreases with increase in temperature depending on the nature of solute. The effect of pressure on the solubility of solids in liquids is generally very small.

On the basis of solubility of solid (solute) in a liquid (solvent), solution may be of the following types

(i) **Unsaturated solution** A solution in which more solute can be dissolved without raising temperature is called an unsaturated solution.
(ii) **Saturated solution** A solution in which no solute can be dissolved further at a given temperature is called a saturated solution.
(iii) **Supersaturated solution** When the solution contains more solute than would be necessary to saturate it, then it is termed as supersaturated solution. Supersaturated solutions are not in equilibrium with the solid substance.

Thus, if a small crystal of solute (say sodium thiosulphate) is added to its supersaturated solution, the excess immediately crystallises out.

Concentration of Solution

The **concentration** of a solution is defined as the relative amount of a solute present in the solution . It is generally expressed as the amount of solute present in a unit volume of solution. Solutions with relatively low concentration are called **dilute solutions,** while those with relatively high concentration are called **concentrated solutions.**

Various expression for the concentrations of solutions can be summarised as

Mass Percentage

It is the amount of solute present in 100 g of the solution.

$$\text{Per cent by mass} = \frac{\text{mass of solute (in g)}}{\text{mass of solution (in g)}} \times 100$$

Volume Percentage

The volume of solute (in mL) present in 100 mL of the solution is called **volume per cent.**

$$\text{Per cent by volume } (v/V) = \frac{\text{volume of solute (in mL)}}{\text{volume of solution (in mL)}} \times 100$$

Mole Fraction (χ)

It is the ratio of the number of moles of one component (i.e. solute or solvent) to the total number of moles of solute and solvent (i.e. moles of solution).

$$\chi_{\text{solute}} = \frac{\text{moles of solute}}{\text{moles of solute + moles of solvent}}$$

$$\chi_{\text{solvent}} = \frac{\text{moles of solvent}}{\text{moles of solute + moles of solvent}}$$

$$\chi_{\text{solute}} + \chi_{\text{solvent}} = 1$$

Example 3. *The vapour pressures of pure liquids A and B are* 400 *and* 600 mmHg*, respectively at* 298 K*. On mixing the two liquids, the sum of their initial volumes is equal to the volume of the final mixture. The mole fraction of liquid B is* 0.5 *in the mixture. The vapour pressure of the final solution, the mole fractions of components A and B in vapour phase, respectively are* ***(JEE Main 2019)***

(a) 450 mmHg, 0.4, 0.6 (b) 500 mmHg, 0.5, 0.5
(c) 450 mmHg, 0.5,0.5 (d) 500 mmHg, 0.4,0.6

Sol. (*d*) According to Dalton's law of partial pressure

$$p_{\text{total}} = p_A + p_B$$

$$= p_A^\circ \chi_A + p_B^\circ \chi_B \quad \ldots\text{(i)}$$

Given, $p_A^\circ = 400$ mm Hg, $p_B^\circ = 600$ mm Hg

$$\chi_B = 0.5, \chi_A + \chi_B = 1$$

$$\therefore \quad \chi_A = 0.5$$

On substituting the given values in Eq. (i) we get,

$$p_{\text{total}} = 400 \times 0.5 + 600 \times 0.5$$

$$= 500 \text{ mm Hg}$$

Mole fraction of A in vapour phase

$$Y_A = \frac{p_A}{p_{\text{total}}} = \frac{p_A^\circ \chi_A}{p_{\text{total}}} = \frac{0.5 \cdot 400}{500} = 0.4$$

mole of B in vapour phase,

$$Y_A + Y_B = 1$$

$$Y_B = 1 - 0.4 = 0.6$$

Parts Per Million (ppm)

When the amount of solute (in g) is present in one million (1 million = 10^6) per mL of solution, the concentration of the solution is expressed in **ppm.**

$$\text{ppm} = \frac{\text{mass of solute (in g)}}{\text{total volume of solution (in mL)}} \times 10^6$$

In case of gases, ppm refers to volumes rather than masses, i.e. 1 ppm means 1 cm^3 of gaseous components is present in 1000 L.

Strength or Concentration in Gram Per Litre

It represents the number of grams present in 1 L of solution.

$$\text{Strength of solution} = \frac{\text{mass of solute (in g)}}{\text{volume of solution (in L)}}$$

Molarity (M)

It is the number of moles of solute present in one litre of the solution.

$$\text{Molarity } (M) = \frac{\text{number of moles of solute}}{\text{volume of solution (in L)}}$$

$$= \frac{\text{mass of solute (in g)}}{\text{mol. wt. of solute} \times \text{volume of solution (in L)}}$$

Molarity varies with temperature due to accompanied change in volume of the solution.

Unit of molarity = mol/L

Relation between molarity and strength in g/L

$$\text{Molarity } (M) = \frac{\text{mass of solute (in g)}}{\text{molecular mass of solute} \times \text{volume of solution (in L)}}$$

$$\text{Molarity } (M) = \frac{\text{strength in g/L}}{\text{molecular mass of solute}}$$

Relation between molarity (M) and mole fraction of the solute (χ)

$$\chi = \frac{MM_1}{M(M_1 - M_2) + d}$$

where, d = density of the solution
M_1 = molar mass of solvent
M_2 = molar mass of solute
M = molarity of solution

Dilution Law on Basis of Molarity

If molarity and volume of solution are changed from M_1, V_1 to M_2, V_2 then

$$M_1V_1 = M_2V_2 \quad \text{(Molarity equation)}$$

If n_1 moles of reactant '1' react with n_2 moles of reactant '2' then $\dfrac{M_1V_1}{n_1} = \dfrac{M_2V_2}{n_2}$

If two solutions of the same solute are mixed then molarity of the resulting solution,

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

Example 4. *Calculate the molarity of* KI *if the density of* 20% *(mass/mass) aqueous* KI *is* 1.202 g mL^{-1}. ***(NCERT)***

(a) 0.04 M
(b) 1.25 M
(c) 0.25 M
(d) 1.45 M

Sol. (*d*) Since density is given, so first we calculate volume and then molarity.

Weight of the solution = 100 g

Density of the solution = 1.202 g mL^{-1}

$$\text{Volume of the solution} = \frac{\text{weight of solution}}{\text{density}}$$

$$= \frac{(100 \text{ g})}{(1.202 \text{ g mL}^{-1})}$$

$$= 83.19 \text{ mL} = 0.083 \text{ L}$$

$$\text{Molarity of the solution } (M) = \frac{\text{number of gram moles of KI}}{\text{volume of solution in litres}}$$

$$= \frac{(20 \text{ g}) / (166 \text{ g mol}^{-1})}{(0.083 \text{ L})}$$

$$= 1.45 \text{ mol L}^{-1} = 1.45 \text{ M}$$

Alternate Method

$$\text{Molarity} = \frac{\% \text{ by mass} \times \text{density} \times 10}{\text{molar mass of KI}}$$

$$= \frac{20 \times 1.202 \times 10}{166} = 1.45 \text{ M}$$

Example 5. 10.30 mg *of* O_2 *is dissolved into a litre of sea water of density* 1.03 g/mL. *The concentration of* O_2 *in ppm is* ***(JEE Main 2020)***

Sol. *(10.00)*

Mass of O_2 = 10.30 mg (Given)

Mass of sea water solution = volume × density

$= 1 \text{ L} \times 1.03 \text{ g/mL}$

$= 1000 \text{ mL} \times 1.03 \text{ g mL}^{-1} = 1030 \text{ g}$

$$\text{ppm} = \frac{\text{mass of } O_2}{\text{mass of solution}} \times 10^6$$

$$= 10 \text{ ppm}$$

Molality (*m*)

It is the number of moles of the solute dissolved in 1000 g of the solvent.

$$\text{Molality } (m) = \frac{\text{number of moles of solute}}{\text{mass of solvent (in g)}} \times 1000$$

$$= \frac{\text{mass of solute (in g)} \times 1000}{\text{molecular weight of solute} \times \text{mass of solvent (in g)}}$$

Molality is independent of temperature.

Unit of molality = g moles/kg of solvent.

Relation between molality and weight percentage of solute (*x*)

$$m = \frac{1000 \times \text{weight \% of solute } (x)}{(100 - x) \times \text{molecular weight of solute}}$$

Relation between molality (*m*) and mole fraction of the solute (χ)

$$\chi = \frac{mM_1}{1 + mM_1}$$

where, M_1 = molecular mass of the solvent

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

$$\text{Molality } (m) = \frac{M}{d - MM_2} \quad \text{(If } d \text{ in kg/L and } M_2 \text{ in kg/mol)}$$

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

(If d in g/L and M_2 in g/mol)

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

where, M_2 = molar mass of the solute
d = density of the solution.

Example 6. *A solution of glucose in water is labelled as* 10% *w/ w. What should be the molality of the solution, if the density of solution is* 1.2 g mL^{-1}? ***(NCERT)***

(a) 0.45 (b) 0.62 (c) 0.82 (d) 0.19

Sol. (*b*) 10% means

W_B = Mass of glucose = 10 g

Mass of solution = 100 g

W_A = Mass of water (solvent)

= 100 − 10 = 90 g = 0.09 kg

M_B = Molar mass of glucose ($C_6H_{12}O_6$)

$= (12 \times 6) + (1 \times 12) + (16 \times 6)$

$= 72 + 12 + 96 = 180 \text{ g mol}^{-1}$

$$\text{Molality of solution } (m) = \frac{W_B/M_B}{W_A} = \frac{(10 \text{ g})/(180 \text{ g mol}^{-1})}{(0.09 \text{ kg})}$$

$$= \frac{(10 \text{ g})}{(180 \text{ g mol}^{-1}) \times (0.09 \text{ kg})}$$

$$= 0.617 \text{ mol kg}^{-1} \text{ or } 0.617 \text{ m}$$

Example 7. *An 'm' molal solution of a compound in benzene has mole fraction of solute equal to* 0.2. *The value of 'm' is*

(a) 0.018 (b) 0.14 (c) 0.040 (d) 0.0032

Sol. (*d*) Mole fraction of solute is given by

$$\chi = \frac{mM_1}{1 + mM_1}$$

where, M_1 = molecular mass of the solvent, i.e. benzene = 78

$$0.2 = \frac{m \times 78}{1 + m \times 78}$$

$$0.2 + 0.2 \times 78\, m = 78\, m$$

or $$(78 - 15.6)\, m = 0.2$$

or $$62.4\, m = 0.2$$

or, $$m = \frac{0.2}{62.4} = 0.0032$$

Normality (N)

Normality is the number of gram equivalents of substance dissolved per litre of the solution.

$$\text{Normality } (N) = \frac{\text{number of gram - equivalent of solute}}{\text{volume of solution (in L)}}$$

$$= \frac{\text{mass of solute (in g)}}{\text{equivalent weight} \times \text{volume (in L)}}$$

$$N = \frac{\text{mass of solute } (w) \text{ (in g)}}{\text{equivalent weight } (E) \times \text{volume } (V) \text{ (in mL)}} \times 1000$$

or $$N = \frac{w \times 1000}{E \times V} \Rightarrow w = \frac{NEV}{1000}$$

Again, Normality (N)

$$= \frac{\text{percent of solute}}{\text{equivalent weight of the solute}} \times 10$$

$$= \frac{\text{weight percent of solute} \times \text{sp. gravity of the solution} \times 10}{\text{equivalent weight of the solute}}$$

Relation between normality and strength in g/L

$$\text{Normality } (N) = \frac{\text{mass of solute (in g)}}{\text{equivalent weight} \times \text{volume (in L)}}$$

$$= \frac{\text{strength in g/L}}{\text{equivalent weight}}$$

Relation between normality and molarity

$$\text{Normality} = \frac{\text{number of g - equivalents of solute}}{\text{volume of solution (in L)}}$$

and, $$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution (in L)}}$$

$$\therefore \quad \frac{\text{Normality}}{\text{Molarity}} = \frac{\text{number of g - equivalent of solute}}{\text{number of moles of solute}}$$

$$= \frac{\text{molecular weight}}{\text{equivalent weight}}$$

$$\Rightarrow \text{normality} \times \text{equivalent weight} = \text{molarity} \times \text{molecular weight}$$

For an acid, $$\frac{\text{molecular weight}}{\text{equivalent weight}} = \text{basicity}$$

$$\therefore \quad \text{Normality of an acid} = \text{molarity} \times \text{basicity}$$

For a base, $$\frac{\text{molecular weight}}{\text{equivalent weight}} = \text{acidity}$$

$$\therefore \quad \text{Normality of a base} = \text{molarity} \times \text{acidity}$$

Relation between normality and percentage of solute

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

where, x = % of the solute by mass

d = density of solution in g/mL

E = equivalent mass of solute

Dilution Law on Basis of Normality

If normality and volume of solution are changed from N_1, V_1 to N_2, V_2 then

$$N_1V_1 = N_2V_2 \text{ (Normality equation)}$$

If n_1 moles of reactant '1' react with n_2 moles of reactant '2', then

$$\frac{N_1V_1}{n_1} = \frac{N_2V_2}{n_2}$$

If two solutions of the same solute are mixed then normality of the resulting solution,

$$N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

Volume of water added to get a solution of normality N_2 from V_1 mL of normality N_1 is

$$V_2 - V_1 = \left(\frac{N_1 - N_2}{N_2}\right) V_1$$

Normality changes with temperature since it involves volume. When a solution is diluted x times, its normality also decreased by x times.

Unit of normality = gram equivalents per litre.

Example 8. *What will be the normality of a solution obtained by mixing* 0.45 N *and* 0.60 N NaOH *in the ratio* 2 :1 *by volume ?*

(a) 0.15 N (b) 0.8 N
(c) 0.5 N (d) 0.45 N

Sol. (c) g-equivalents $= 0.45 \times 2V + 0.60 \times V$

Total volume $= 2V + V = 3V$

$\Rightarrow$ g-equivalents of NaOH solution obtained $= N \times 3V$

$$\therefore \quad N \times 3V = 0.45 \times 2V + 0.6V$$

$$3NV = 0.9V + 0.6V$$

$$N = \frac{1.5V}{3V} = \frac{1}{2} = 0.5$$

Formality (F)

This is the concentration unit for ionic compounds which dissolve in a polar solvent to give pair of ions. This represents number of gram-formula weight of the substance dissolved per litre of the solution. It is almost the same as molarity. It describes the solute that is mixed in a liquid rather than the solute present in solution after the dissolution process.

$$\text{Formality} = \frac{\text{moles of substance added to solution}}{\text{volume of solution (in L)}}$$

If formula weight is equal to molecular weight, formality and molarity will be same.

Formality is also dependent on temperature.

Demal (D)

It is equal to molar concentration at 0°C, i.e. 1D represents one mole of the solute present in one litre of the solution at 0°C.

Remember Normality and molarity changes with temperature because these involve volumes while molality, mole fraction and mass fraction do not change with temperature because they involve weights.

Vapour Pressure of Solutions and Raoult's Law

The pressure exerted by the vapours of a solvent while in equilibrium with pure solvent, at a given temperature, is called vapour pressure.

Factors Affecting Vapour Pressure

Vapour pressure gets affected by following factors

(i) **Purity of the liquid** Pure liquid always has a vapour pressure higher than its solution.

(ii) **Nature of the liquid** Liquids which have weak intermolecular forces are volatile and have greater vapour pressure.

(iii) **Temperature** The vapour pressure of a liquid increases with increase in temperature. This is because on increasing the temperature the kinetic energy of molecules increases that results into the fact that more molecules of the liquid can go into vapour phase.

(iv) **Effect of adding non-volatile solute** When a liquid contains a non-volatile solute, some of the solvent molecules are replaced by the solute particles on the liquid surface and therefore, the available surface area for the escape of solvent molecule decreases.

Due to the less available area on the surface of liquid for escape, rate of evaporation and hence, the rate of condensation both lowers.

The vapour pressure of liquid in solution is known as its **partial vapour pressure** and is less than the vapour pressure of the pure liquid at the same temperature.

If $p°$ be the vapour pressure of pure liquid and p_s be that of liquid in solution then lowering of vapour pressure of the liquid = $p° - p_s$

$\therefore$ Relative lowering in pressure = $\dfrac{p° - p_s}{p°}$

Raoult's Law

Raoult's law states, "For a solution of two miscible liquids, the vapour pressure of each liquid in the solution is less than the respective vapour pressure of the pure liquid and at the equilibrium, partial vapour pressure of the liquid is directly proportional to its mole fraction in solution."

For a solution containing two liquids A and B, the partial vapour pressure of liquid A is

$$p_A \propto \chi_A \quad \text{or} \quad p_A = k\chi_A$$

where, $\chi_A = \dfrac{n_A}{(n_A + n_B)}$ = the **mole fraction of liquid A**

The proportionality constant k is obtained by considering the pure liquid when $\chi_A = 1$, then $k = p_A^\circ$, (the vapour pressure of pure liquid), hence,

$$p_A = p_A^\circ \chi_A$$

Similarly,
$$p_B = p_B^\circ \chi_B$$

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

$$p_{\text{total}} = p_A + p_B$$

Substituting the values of p_A and p_B, we get

$$\begin{aligned} p_{\text{total}} &= \chi_A p_A^\circ + \chi_B p_B^\circ \\ &= (1 - \chi_B) p_A^\circ + \chi_B p_B^\circ \\ &= p_A^\circ + (p_B^\circ - p_A^\circ)\chi_B \end{aligned}$$

Following conclusions can be drawn from the equation

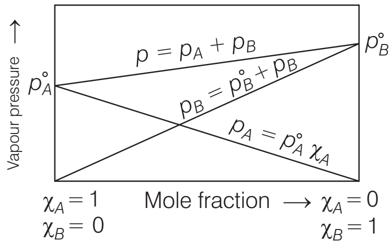
- Total vapour pressure over the solution can be related to the mole fraction of any one component.
- Total vapour pressure over the solution varies linearly with the mole fraction of component B.
- Depending on the vapour pressures of the pure components A and B, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component.

The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If y_1 and y_2 are the mole fractions of the component 1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressures :

$$p_1 = y_1 \, p_{\text{total}}$$
$$p_2 = y_2 \, p_{\text{total}}$$

In general, $p_i = y_i \; p_{\text{total}}$

Also in other words the vapour pressure of a solution containing non-volatile solute is directly proportional to the mole fraction of the solvent.



Relationship of vapour pressure and mole fraction of an ideal solution at constant (Raoult's law is being followed).

Raoult's Law as a Special Case of Henry's Law

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $p_i = x_i \; p_i^\circ$. In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and we have already seen that its solubility is given by Henry's law which states that

$$p = K_H x$$

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial presssure of the volatile component or gas is directly proportional to its mole fraction in the solution. Only the proportionality constant K_H differs from p_i°,

Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_i°.

Example 9. *Heptane and octane form an ideal solution. At* 373 K*, the vapour pressure of the two liquid components are* 105.2 kPa *and* 46.8 kPa *respectively. What will be the vapour pressure of a mixture of* 26.0 g *of heptane and* 35 g *of octane?* ***(NCERT)***

(a) 82.8 kPa (b) 73.5 kPa (c) 39.2 kPa (d) 88.2 kPa

Sol. (*b*) Number of moles of octane

$$(n_A) = \frac{\text{Mass}}{\text{Molar mass}} = \frac{35 \text{ g}}{114 \text{ g mol}^{-1}} = 0.307 \text{ mol}$$

[Molar mass of octane

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

Number of moles of heptane

$$(n_B) = \frac{26 \text{ g}}{100 \text{ g mol}^{-1}} = 0.26 \text{ mol}$$

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

Mole fraction of octane

$$(\chi_A) = \frac{n_A}{n_A + n_B} = \frac{(0.307 \text{ mol})}{(0.307 + 0.26) \text{ mol}} = 0.541$$

Mole fraction of heptane

$$(\chi_B) = \frac{n_B}{n_A + n_B} = \frac{(0.26 \text{ mol})}{(0.307 + 0.26) \text{ mol}} = 0.458$$

Vapour pressure of pure heptane $(p_B^\circ) = 105.2$ kPa

Vapour pressure of pure octane $(p_A^\circ) = 46.8$ kPa

In the mixture of 26.0 g heptane and 35.0 g octane

(i) Vapour pressure of heptane $(p_B) = p_B^\circ \; \chi_B$

$$= (105.2 \text{ kPa} \times 0.458)$$
$$= 48.18 \text{ kPa}$$

(ii) Vapour pressure of octane

$$(p_A) = p_A^\circ \; \chi_A = (46.8 \text{ kPa} \times 0.541) = 25.32 \text{ kPa}$$

(iii) Total vapour pressure of the mixture

$$(p) = p_A + p_B$$
$$= 25.32 + 48.18 = 73.5 \text{ kPa}$$

Example 10. *The vapour pressure of chloroform* ($CHCl_3$) *and dichloromethane* (CH_2Cl_2) *at* 298 K *is* 200 mm Hg *and* 415 mm Hg, *respectively. If a solution is prepared by mixing* 25.5 g *of* $CHCl_3$ *and* 40 g *of* CH_2Cl_2 *at* 298 K, *calculate the mole fractions of chloroform in vapour phase.* ***(NCERT Exemplar)***

(a) 0.18 (b) 0.82 (c) 0.34 (d) 0.48

Sol. (*a*) Molar mass of $CH_2Cl_2 = 12 \times 1 + 1 \times 2 + 35.5 \times 2$

$$= 85 \text{ g mol}^{-1}$$

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

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

$$\text{Moles of } CH_2Cl_2 = \frac{40 \text{ g}}{85 \text{ g mol}^{-1}} = 0.47 \text{ mol}$$

$$\text{Moles of } CHCl_3 = \frac{25.5 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.213 \text{ mol}$$

Total number of moles = 0.47 + 0.213 = 0.683 mol

$$\chi_{CH_2Cl_2} = \frac{0.47 \text{ mol}}{0.683 \text{ mol}} = 0.688$$

$$\chi_{CHCl_3} = 1.00 - 0.688 = 0.312$$

$$p_{\text{total}} = p^\circ_{CHCl_3} + (p^\circ_{CH_2Cl_2} - p^\circ_{CHCl_3}) \; \chi_{CH_2CH_2}$$
$$= 200 + (415 - 200) \times 0.688$$
$$= 347.9 \text{ mmHg}$$

To calculate the mole fraction of component in vapour phase,

$$\chi_i^V = p_i / p_{\text{total}}$$

$$\therefore \quad p_{CH_2Cl_2} = 0.688 \times 415 \text{ mmHg} = 285.5 \text{ mmHg}$$

$$p_{CHCl_3} = 0.312 \times 200 \text{ mmHg} = 62.4 \text{ mmHg}$$

$$\chi^V_{CH_2Cl_2} = \frac{285.5}{347.9} = 0.82 \text{ and } \chi^V_{CHCl_3} = \frac{62.4}{347.9} = 0.18$$

Note Since, CH_2Cl_2 is more volatile component than $CHCl_3$ [$p^\circ_{CH_2Cl_2} = 415$ mm Hg and $p^\circ_{CHCl_3} = 200$ mm Hg] and the vapour phase is also richer in CH_2Cl_2 [$\chi^V_{CH_2Cl_2} = 0.82$ and $\chi^V_{CHCl_3} = 0.18$], it may be concluded that at equilibrium, vapour phase will be always rich in the component which is more volatile.

Limitations of Raoult's Law

- It is applicable only to very dilute solutions as in case of non-dilute solutions there occur strong interactions between solute and solvent molecules which causes either positive or negative deviations.
- It is applicable only to solutions containing non-volatile and non-electrolytic solutes which exist as a single molecule.
- It is not applicable to solutes which dissociate or associate in the particular solution.

Ideal Solutions

Ideal solutions are those, which obey Raoult's law over the entire range of concentration at a given temperature. The total vapour pressure of an ideal solution containing components A and B is given by

$$p = p_A + p_B = p_A^\circ \chi_A + p_B^\circ \chi_B$$

In an ideal solution of two components say A and B, all cohesive forces (A—A, B—B and A—B) must be identical.

- both have similar structure,
- both have similar molecular sizes,
- both have identical intermolecular forces.

Examples of the ideal solutions are

Benzene-toluene, n-hexane-n-heptane; ethyliodide-ethyl bromide, chlorobenzene- bromobenzene.

Characteristics of an Ideal Solution

The mixture of two liquids results in an ideal solution when

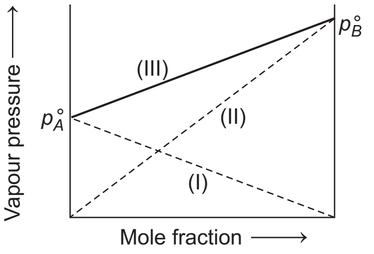
(i) These obey Raoult's law.

(ii) $\Delta H_{\text{mixing}} = 0$, i.e. no energy evolved or absorbed on mixing.

(iii) $\Delta V_{\text{mixing}} = 0$, i.e. on mixing no expansion or contraction occurs.

Graphical Representation of Ideal Solutions

The curve I (straight line) gives variations of vapour pressure of liquid A and the curve II gives that of liquid B with their respective mole fractions.



Vapour pressure behaviour of ideal solutions obeying Raoult's law

The resultant graph III (representing $p = p_A{}^\circ \chi_A + p_B{}^\circ \chi_B$) is the plot for solution and is a straight line joining $p_A{}^\circ$ and $p_B{}^\circ$. Hence, the vapour pressure at various compositions of ideal solutions is intermediate between the values of $p_A{}^\circ$ and $p_B{}^\circ$.

Non-Ideal or Real Solutions

Solutions, which do not obey Raoult's law, are called non-ideal solutions. Hence, for such solutions $p_A \neq p_A^\circ \chi_A$ and $p_B \neq p_B^\circ \chi_B$.

For such mixtures,

$$\Delta H_{\text{mixing}} \neq 0$$

and $$\Delta V_{\text{mixing}} \neq 0;$$

Non-ideal solutions show the following two types of deviations from ideal behaviour

1. Solution Showing Positive Deviation

The vapour pressure of each component in such a mixture is more than what would be expected on the basis of Raoult's law of components A and B alone.

If the attraction between A and B molecules is less than the attractive forces between A to A and B to B, the escaping tendency in solution is higher than in either of the pure components.

For such a deviation

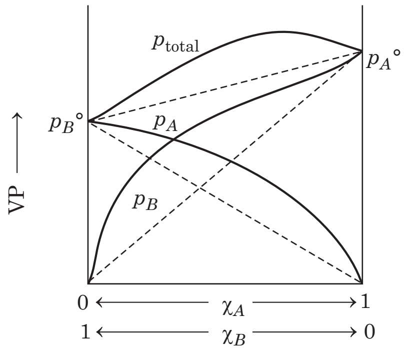
$$p_A > p_A{}^\circ \chi_A \ , \ p_B > p_B{}^\circ \chi_B$$

and hence, $$p_{\text{total}} > p_A{}^\circ \chi_A + p_B{}^\circ \chi_B$$

also $$\Delta H_{\text{mixing}} > 0$$

as the new bonds formed are weaker and energy is absorbed.

$\Delta V_{\text{mixing}} > 0$, i.e. there is increase in volume.



Graph of solution showing positive deviation from Raoult's law

e.g. Ethanol-water, ether-acetone, carbon disulphide-acetone, carbon tetrachloride-methanol, cyclohexane-ethanol, water-methanol, carbon tetrachloride-benzene, carbon tetrachloride-toluene, acetone-benzene.

2. Solutions Showing Negative Deviation

For such solutions, the partial vapour pressure of each component is less than what would be expected on the basis of Raoult's law.

In such a mixture, the attraction between molecules of A and B is greater than the force between A—A molecules or B—B hence the escaping tendencies of both the components are lowered.

For a mixture showing negative deviation

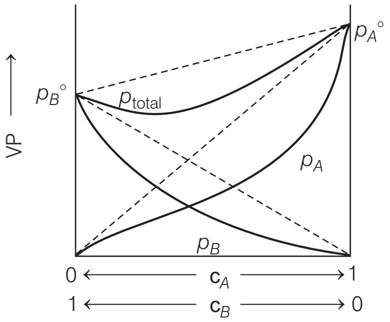
$$p_A < p_A^\circ \chi_A$$

or $$p_B < p_B^\circ \chi_B,$$

hence, $$p_{\text{total}} < p_A^\circ \chi_A + p_B^\circ \chi_B$$

$\Delta H_{\text{mixing}} < 0$, i.e. heat is evolved due to the formation of stronger bonds.

$\Delta V_{\text{mixing}} < 0$, i.e. there is decrease in volume.



Graph of solution showing negative deviation from Raoult's law

e.g. Acetic acid-methanol, acetic acid-pyridine acetone-aniline, acetone-chloroform, benzene-chloroform, water-hydrochloric acid, water-nitric acid etc.

Comparison between Ideal and Non-Ideal Solutions

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	**Negative deviation from Raoult's law**
Each component obeys Raoult's law at all temperature and pressure, i.e. $p_A = p_A^\circ \chi_A$ and $p_B = p_B^\circ \chi_B$	Their components do not obey Raoult's law. i.e. $p_A > p_A^\circ \chi_A$ and $p_B > p_A^\circ \chi_B$	Their components do not obey Raoult's law, i.e. $p_A < p_A^\circ \chi_A$ and $p_B < p_B^\circ \chi_B$
$\Delta_{\text{mix}} V = 0, \Delta_{\text{mix}} H = 0$	$\Delta_{\text{mix}} V > 0, \Delta_{\text{mix}} H > 0$ (endothermic)	$\Delta_{\text{mix}} V < 0, \Delta_{\text{mix}} H < 0$ (exothermic)
Intermolecular interactions, i.e. A—B interactions are same as present in pure components, i.e. A—A or B—B.	Intermolecular interactions, i.e. A—B interactions are weaker than in pure components, i.e. between A—A or B—B	Intermolecular interactions, i.e. A—B interactions are stronger than in pure components, i.e. between A—A or B—B.
e.g. Benzene + toluene, *n*-hexane + *n*-heptane; chlorobenzene + bromobenzene; ethyl bromide + ethyl iodide; *n*-butyl chloride + *n*-butyl bromide.	e.g. Ethanol + water, ether + acetone, acetone + benzene, carbon disulphide + acetone, carbon tetrachloride + methanol, cyclohexane + ethanol, water + methanol, carbon tetrachloride +benzene.	e.g. Acetic acid + methanol, acetic acid + pyridine, acetone + aniline, acetone + chloroform, benzene + chloroform, water + hydrochloric acid, water + nitric acid.

Azeotropic Mixtures

A mixture of two liquids which boils at a constant temperature and distils over without any change in composition is called azeotropic mixture.

Azeotropic mixtures are of two types

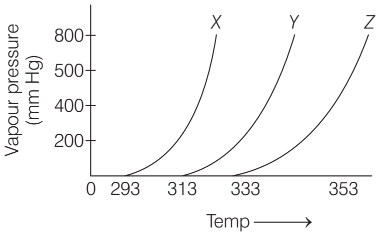
1. **Minimum boiling azeotropes** These are the mixture of two liquids boiling point of which is less than either of the two pure components. These are formed by non-ideal solutions showing positive deviations.
2. **Maximum boiling azeotropes** These are the mixtures of two liquids boiling point of which is more than either of the two pure components.

   These are formed by non-ideal solutions showing negative deviations.

Some Azeotropic Mixtures

Components		**Composition**	**Boiling point** (K)		
A	***B***	(mass % B)	***A***	***B***	**Azeotrope**
Minimum Boiling Azeotropes					
H_2O_2	C_2H_5OH	95.6	373	351.5	351
H_2O	n-C_3H_7OH	72.0	373	370.2	361
$CHCl_3$	C_2H_5OH	6.8	334.2	351.3	223.3
Maximum Boiling Azeotropes					
H_2O	HCl	20.2	373	188	381.6
H_2O	HNO_3	68.0	373	359	393.5
H_2O	HCOOH	77.0	373	374	380.0
$CHCl_3$	CH_3COCH_3	20.0	334.2	329.1	337.7

Example 11. *A graph of vapour pressure and temperature for three different liquids X, Y, and Z is shown below :*



The following inference are made ***(JEE Main 2020)***

A. X has higher intermolecular interactions compared to Y.
B. X has lower intermolecular interactions compared to Y.
C. Z has lower intermolecular interactions compared to Y.

The correct inference(s) is/are

(a) (C) (b) (B)
(c) (A) (d) (A) and (C)

Sol. (*b*) From given graph it can be seen that, X has higher vapour pressure as compared to Y at lower temperature (or to attain same vapour pressure, Y need higher temeprature than X). It means that intermolecular interaction must be weaker in X as compared to Y, which further must be weaker than Z by the same reason also. Hence, option (b) is correct.

Example 12. *A 4% solution of sucrose* $C_{12}H_{22}O_{11}$ *is isotonic with 3% solution of an unknown organic substance. The molecular mass of the unknown substance will be*

(a) 2.565 g (b) 25.65 g
(c) 256.5 g (d) 2565 g

Sol. (c) Since the two solutions are isotonic, they must have same concentrations in moles/litre.

For sucrose solution, we have concentration

$$= 4 \text{ g}/100 \text{ cm}^3 \text{ (given)}$$

$$= 40 \text{ g L}^{-1} = \frac{40}{342} \text{mol L}^{-1}$$

(Molecular mass of sucrose $C_{12}H_{22}O_{11} = 342$)

For unknown substance, suppose m is the molecular mass, then concentration = 3 g/100 cm^3 (given)

$$= 30 \text{ g L}^{-1} = \frac{30}{Mw} \text{ mol L}^{-1}$$

Thus, we have $\frac{30}{Mw} = \frac{40}{342}$

$$Mw = \frac{30 \times 342}{40} = 256.5$$

Colligative Properties

The properties of a dilute solution which depends only upon the number of particles present in a solution and their concentration are called colligative properties. These does not depend on the chemical nature of solute. These are proportional to the number of solute particles in the solution.

Factors affecting colligative properties are as follows

- Fraction of solute and solvent particles in solution.
- Nature of solvent.
- Extent of association and dissociation of solute particles in solution.

There are four colligative properties are as follows

- Relative lowering of vapour pressure
- Elevation in boiling point
- Depression in freezing point
- Osmotic pressure

Relative Lowering of Vapour Pressure

When a non-volatile solute is added to a solvent, the vapour pressure is lowered. So, vapour pressure of a solution (p) is always less than the vapour pressure of pure solvent (p°) at that temperature. Therefore, ($p^\circ - p$) is called the **lowering in vapour pressure** and the ratio $\left(\frac{p^\circ - p}{p^\circ}\right)$ is known as the **relative lowering in vapour pressure.**

According to **Raoult's law,** "the relative lowering in vapour pressure of a dilute solution is equal to the mole fraction of the solute present in the solution. i.e.

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

where, χ_B = mole fraction of solute

Determination of Molecular Mass

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

Then, according to Raoult's law,

$$\therefore \quad \frac{p^\circ - p_s}{p^\circ} = \frac{n}{n+N}$$

$$\frac{p^\circ - p_s}{p^\circ} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}} \quad \left[\because n = \frac{w}{m} \text{ and } N = \frac{W}{M}\right]$$

For very dilute solutions,

$$n <<< N$$

$$\therefore \quad \frac{p^\circ - p_s}{p^\circ} = \frac{n}{N}$$

$$\text{or} \quad \frac{p^\circ - p_s}{p^\circ} = \frac{w \times M}{m \times W}$$

This expression is used to find the molecular weight of an unknown solute dissolved in a given solvent.

Alternate Formula for the Relative Lowering of Vapour Pressure (When the solution is not Dilute)

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_B}{n_A + n_B} \qquad \ldots\text{(i)}$$

On reversing Eq. (i), we get

$$\frac{p^\circ}{p^\circ - p_s} = \frac{n_A + n_B}{n_B} = 1 + \frac{n_A}{n_B}$$

$$\Rightarrow \qquad \frac{p^\circ}{p^\circ - p_s} - 1 = \frac{n_A}{n_B}$$

$$\Rightarrow \qquad \frac{p^\circ - p^\circ + p_s}{p^\circ - p_s} = \frac{n_A}{n_B} \quad \Rightarrow \quad \frac{p_s}{p^\circ - p_s} = \frac{n_A}{n_B}$$

$$\text{or} \qquad \boxed{\frac{p^\circ - p_s}{p_s} = \frac{n_B}{n_A}}$$

Example 13. *Calculate the mass of a non-volatile solute (molar mass* 40 g mol^{-1}*) which should be dissolved in* 114 g *octane to reduce its vapour pressure to* 80%.

(a) 20 g (b) 10 g (c) 30 g (d) 45 g

Sol. (*b*) According to Raoult's law, relative lowering of vapour pressure,

$$\frac{p_A^\circ - p_S}{p_A^\circ} = \chi_B \qquad \ldots\text{(i)}$$

$$\chi_B = \frac{n_B}{n_B + n_A} = \frac{W_B/M_B}{\dfrac{W_B}{M_B} + \dfrac{W_A}{M_A}} \qquad \ldots\text{(ii)}$$

Given vapour pressure is reduced to 80% when non-volatile solute is dissolved in octane. It means

If $p_A^\circ = 1$ atm then $p_S = 0.8$ atm; $p_A^\circ - p_S = 0.2$ atm;

M_A (C_8H_{18}) = 114 g mol^{-1}; $W_A = 114$ g; $M_B = 40$ g mol^{-1}; $W_B = ?$

Applying Eq. (ii)

$$\frac{0.2}{1} = \frac{W_B/40}{\dfrac{W_B}{40} + \dfrac{114}{114}} = \frac{W_B/40}{\dfrac{W_B}{40} + 1}$$

$$0.2 = \frac{W_B}{W_B + 40}$$

$$0.2W_B + 8 = W_B$$

$$W_B = 10$$

Example 14. *The vapour pressure of* 100 g *water reduces from* 17.53 mm *to* 17.22 mm *when* 17.10 g *substance 'X' is dissolved in it. Substance X can be*

(a) methanol (b) glucose

(c) carbon dioxide (d) cannot predict

Sol. (*b*) $\dfrac{p^\circ - p_s}{p^\circ} = \dfrac{n}{n+N} = \dfrac{\dfrac{w}{m}}{\dfrac{w}{m} + \dfrac{W}{M}}$

$$\because \qquad \frac{w}{m} <<< \frac{W}{M}$$

$$\therefore \qquad \frac{p^\circ - p_s}{p^\circ} = \frac{w/m}{W/M} = \frac{w}{m} \times \frac{M}{W}$$

$$\Rightarrow \qquad \frac{17.53 - 17.22}{17.53} = \frac{17.10}{m} \times \frac{18}{100}$$

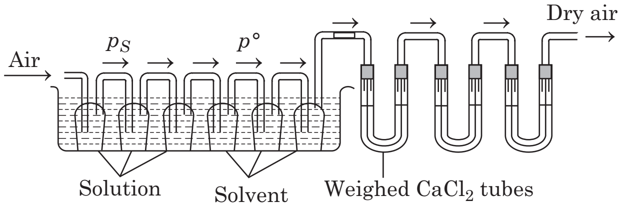
$$\Rightarrow \qquad m = \frac{17.10 \times 18 \times 17.53}{0.31 \times 100}$$

$$m = 174.05$$

174 is nearest to the molecular weight of glucose ($C_6H_{12}O_6$), thus the substance 'X' can be glucose.

Experimental Method of Calculation of Relative Lowering in Vapour Pressure

The experimental setup for determining relative lowering in vapour pressure is shown in the figure. It consists of two sets of bulbs. The first set of three bulbs is filled with solution, to half of their capacity and the second set of another three bulbs is filled with the pure solvent.



Ostwald and Walker method

Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes which contain anhydrous calcium chloride or some other dehydrating agents such as P_2O_5, concentrated H_2SO_4, etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

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

$$\frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}} = \frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

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

For very dilute solutions, the following relationship can be applied

$$\frac{p^\circ - p_s}{p^\circ} = \frac{\text{loss in mass in solvent bulbs}}{\text{gain in mass of guard tubes}} = \frac{W_B/M_B}{W_A/M_A}$$

Example 15 *A current of dry air was bubbled through a bulb containing* 26.66 g *of an organic compound in* 200 g *of water, then through a bulb at the same temperature, containing water and finally through a tube containing anhydrous calcium chloride. The loss of mass in the bulb containing water was* 0.087 g *and the gain in the mass of calcium chloride tube was* 2.036 g. *Calculate the molecular mass of the organic substance.*

(a) 35.23 (b) 53.75 (c) 40.21 (d) 21.15

Sol. (*b*) $\frac{p^\circ - p_s}{p^\circ} = \frac{\text{loss in the mass of solvent bulb}}{\text{gain in the mass of CaCl}_2\text{ tube}} = \frac{0.087}{2.036}$

Let the molecular mass of the organic substance be M_2.

According to Raoult's law,

$$\frac{p^\circ - p_s}{p^\circ} = \frac{W_2/M_2}{\frac{W_2}{M_2} + \frac{W_1}{M_1}}$$

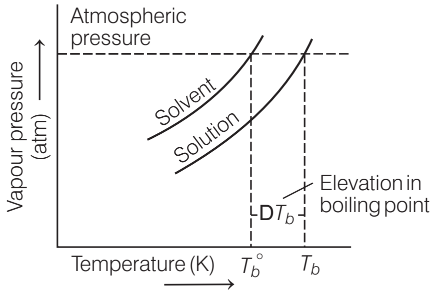
$$\frac{0.087}{2.036} = \frac{\frac{26.66}{M_2}}{\frac{26.66}{M_2} + \frac{200}{18}} = \frac{26.66}{26.66 + \frac{200}{18}M_2}$$

$$M_2 = 53.75 \text{ g mol}^{-1}$$

Elevation in Boiling Point of the Solvent (Ebullioscopy)

The boiling point of a liquid may be defined as the temperature at which vapour pressure becomes equal to the atmospheric pressure (760 mm). As the vapour pressure of a solution is decreased due to the presence of a non-volatile solute, the solution boils at a higher temperature as compared to the pure solvent.

The boiling point of the solution is therefore higher than the boiling point of the pure solvent. If T_b° is the boiling point of pure liquid and T_b is the boiling point of solution then,



Elevation in boiling point

Elevation in boiling point, $\Delta T = T_b - T_b^\circ$

The elevation in boiling point is proportional to the molality of the solution, i.e.

$$\Delta T_b \propto m \quad \text{or} \quad \Delta T_b = k_b m$$

Determination of Molecular Mass from Elevation in Boiling Point

We know that molality,

$$m = \frac{\text{weight of solute} \times 1000}{\text{mol. wt. of solute} \times \text{mass of solvent}} = \frac{w \times 1000}{m' \times W}$$

On putting the value of m in expression of elevation in boiling point, we get

$$\text{or} \qquad \Delta T_b = \frac{k_b \times w \times 1000}{m' \times W}$$

$$\text{or} \qquad m' = \frac{k_b \times w \times 1000}{\Delta T_b \times W}$$

where, k_b = molal boiling point elevation constant or ebullioscopic constant of the solvent

w = weight of the solute

W = weight of solvent

m' = molecular weight of the solute

Sometimes the value of k_b is given per 0.1 kg (100 g), in such case the expression becomes

$$m = \frac{100 \times k_b \times w}{\Delta T_b \times W}$$

k_b is defined as the elevation in boiling point produced when 1 mole of the solute is dissolved in 1 kg of the solvent.

Unit of k_b $= \text{K (mol/kg)}^{-1}$

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

Molal boiling point elevation constant (k_b) can be calculated from molar enthalpy of vaporisation (ΔH_{vap}) of the solvent using the expression,

$$k_b = \frac{MR(T_b^\circ)^2}{(\Delta H_{\text{vap}} \times 1000)}$$

where, M = molar mass of solvent,

T_b° = boiling point of solvent

R = gas constant .

Molal boiling point elevation constant (k_b) can also be calculated from latent heat of evaporation (l_v) of pure solvent using the expression.

$$k_b = \frac{0.002(T^\circ)^2}{l_v}$$

where, T° = normal boiling point of the pure solvent

l_v = latent heat of evaporation in cal/g of pure solvent

Example 16. *Calculate the boiling point of a solution containing* 0.456 g *of camphor (molar mass* = 152*) dissolved in* 31.4 g *of acetone (*= 56.30°C*), if the molecular elevation constant per* 100 g *of acetone is* 17.2°C.

(a) 56.46°C
(b) 36.56°C
(c) 56.14°C
(d) 72.52°C

Sol. (*a*) We know that

$$\Delta T_b = \frac{100k_b \times w}{W \times m'} = \frac{100 \times 17.2 \times 0.456}{31.4 \times 152}$$

$$= 0.16^\circ \text{ C}$$

∴ Boiling point of solution $(T_s) = T^\circ + \Delta T_b$

$$= 56.30 + 0.16$$

$$= 56.46^\circ \text{ C}$$

Example 17 *The elevation of boiling point of* 0.10 m *aqueous* $CrCl_3 \cdot xNH_3$ *solution is two times that of* 0.05 m *aqueous* $CaCl_2$ *solution. The value of x is ....*

[Assume 100% *ionisation of the complex and* $CaCl_2$*, coordination number of* Cr *as* 6*, and that all* NH_3 *molecules are present inside the coordination sphere]*

(JEE Main 2020)

Sol. *(5.00)*

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

For $CaCl_2$, $i = 3$, $m_{(CaCl_2)} = 0.05$ m

∴ $\Delta T_b = 3 \times 0.05 \times K_b = 0.15K_b$

Molality of $CrCl_3 \cdot xNH_3 = 0.1$ m

∴ $\Delta T'_b = i \times m \times K_b = 0.1\, iK_b$

Given that : $0.1\, iK_b = 2 \times 0.15 \times K_b$

∴ $i = 3$ and coordination number is 6.

Thus, complex will be $[Cr(NH_3)_5Cl]Cl_2$

∴ $x = 5$

Hence, the correct answer is 5.

Depression in Freezing Point of the Solvent (Cryoscopy)

The temperature at which the liquid and solid states of a substance have the same vapour pressure is called **freezing point**.

Since, the vapour pressure of a solvent is lowered by the addition of non-volatile solute, the freezing point of the solution (T_f) is always lower than the freezing point of the pure solvent (T_f°).

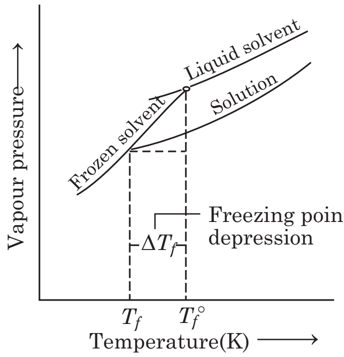
Therefore, depression in freezing point, $\Delta T_f = T_f^\circ - T_f$

The depression in freezing point is proportional to the molality of the solution, i.e.

$$\Delta T_f \propto m$$

or $$\boxed{\Delta T_f = k_f m}$$

where, k_f = molal freezing point depression constant or cryoscopic constant of the solvent



Depression in freezing point graph

Determination of Molecular Mass from Depression in Freezing Point

As we known, molality, $m = \dfrac{w \times 1000}{m' \times W}$

On putting this value in the expression of depression in freezing point, we get

$$\Delta T_f = \frac{k_f \times w \times 1000}{m' \times W} \quad \text{or} \quad m' = \frac{k_f \times w \times 1000}{\Delta T_f \times W}$$

where, w = weight of the solute
W = weight of the solvent
m' = molecular weight of the solute

Sometimes the value of k_f is given per 0.1 kg (100 g), in such case the expression becomes

$$m' = \frac{100 \times k_f \times w}{\Delta T_f \times W}$$

k_f is defined as the depression in freezing point produced when 1 mole of the solute is dissolved in 1 kg of the solvent.

Unit of k_f $= \text{K (mol/kg}^{-1}) = \text{K kg - mol}^{-1}$

Molal depression constant, k_f can be calculated from molar heat of fusion of the solvent using the expression

$$k_f = \frac{MR\,(T_f^\circ)^2}{(\Delta H_{\text{fusion}} \times 1000)}$$

where, M = molar mass of solvent,
$T_f{}^\circ$ = boiling point of solvent
R = gas constant

Molal freezing point depression constant (k_f) can also be calculated from latent heat of fusion (l_f) of pure solvent using the expression

$$k_f = \frac{0.002\,(T^\circ)^2}{l_f}$$

where, T° = normal freezing point of the solvent
l_f = latent heat of fusion in cal/g of pure solvent

Some Practical Applications of Depression of Freezing Point

(i) **Antifreeze solutions** Water is used in radiators of vehicles as cooling liquid. If the vehicle is to be used at high altitudes where the temperature is sub-zero, water would freeze in the radiators. To avoid this difficulty, a solution of ethylene glycol in water is used in radiators. This solution has freezing point lower than zero.

Freezing point can be lowered to the desired extent by changing the concentration. With proper ratio of ethylene glycol and water, it is possible to protect the automotive cooling system to temeprature up to – 48°C.

(ii) **Clearing of ice from roads in the hills** Salts such as NaCl or $CaCl_2$ are scattered on icy roads at higher altitudes. This helps in melting the ice as long as the outdoor temeprature is above the lowest freezing point of **salt-water mixture**. NaCl can melt ice at temperature as low as – 21°C. $CaCl_2$ is effective in melting the ice at a temperature as low as – 55°C.

Example 18. *Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5° C. K_f = 3.9 K kg mol^{-1}.* ***(NCERT)***

(a) 5 g (b) 4 g (c) 8 g (d) 9 g

Sol. (a) Mass of ascorbic acid $(W_A) = 75\text{ g} = 0.075\text{ kg}$

Depression in melting point $(\Delta T_f) = 1.5°\text{ C} = 1.5\text{ K}$

Molar mass of ascorbic acid

$$(M_B) = (12\times 6) + (8\times 1) + (16\times 6) = 176\text{ g mol}^{-1}$$

Molal depression constant $(K_f) = 3.9\text{ K kg mol}^{-1}$

Since, lowering of melting point is given, apply the formula for lowering of melting point, i.e.

$$\Delta T_f = K_f \cdot m$$

$$\Delta T_f = \frac{K_f \cdot W_B}{M_B \times W_A} \quad \text{or} \quad W_B = \frac{\Delta T_f \cdot M_B \cdot W_A}{k_f}$$

$$W_B = \frac{(176\text{ g mol}^{-1})\times(1.5\text{ K})\times(0.075\text{ kg})}{(3.9\text{ K kg mol}^{-1})} = 5.08\text{ g}$$

Example 19. *How much amount of* NaCl *should be added to* 600 g *of water* ($\rho = 1.00$ g/mL) *to decrease the freezing point of water to* -0.2°C? …… *(The freezing point depression constant for water* = 2 K kg mol^{-1}) ***(JEE Main 2020)***

Sol. *(1.76)* $\Delta T_f = i \times m \times K_f = \dfrac{i \times K_f \times w_{\text{NaCl}} \times 1000}{\underset{(=58.5)}{M_{\text{NaCl}}} \times w_{H_2O}}$

$$(m = \text{molality}) = \frac{w_B \times 1000}{M_B \times w_A}$$

$\Delta T_f = 0.2$ because freezing point

$= -0.2$°C; K_f of water $= 2$ K kg mol^{-1} (Given)

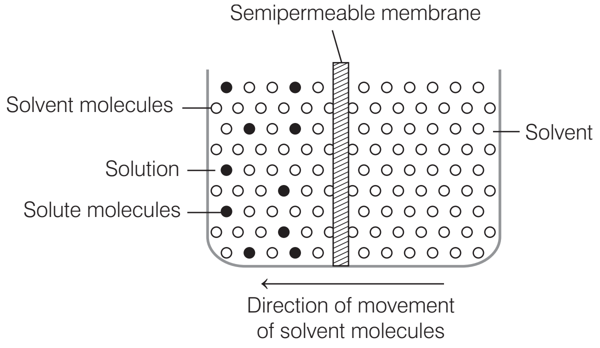
i = van't Hoff factor, for NaCl = 2

$$\therefore \quad w_{\text{NaCl}} = \frac{\Delta T_f \times M_{\text{NaCl}} \times w_{H_2O}}{i \times K_f \times 1000}$$

$$= \frac{0.2 \times 58.5 \times 600}{2 \times 2 \times 1000} = 1.755\text{ g} \approx 1.76\text{ g}$$

Osmosis

It is the spontaneous flow of the solvent molecules through semipermeable membrane pure to the solution side or from a dilute to a concentrated solution.



Semipermeable Membranes

These are thin sheets, which allow the passage of only solvent molecules through them, e.g. egg membrane, goat's bladder, cell membrane are natural semipermeable membranes.

Artifical membranes of gelatinous inorganic substances such as calcium phosphate, copper ferrocyanide, freshly prepared silicates of iron, cobalt nickel etc., are also semipermeable. Cellophane and perchment papers etc., are also used for the same purpose.

Difference between Osmosis and Diffusion

- Diffusion is intermingling of molecules or ion etc., resulting from the random thermal agitation thus there is no restriction to motion of any kind of particles while in osmosis only solvent molecules flow.
- Osmosis takes place through a semipermeable membrane while for diffusion it is not required.
- A homogeneous mixture is obtained as a result of diffusion. On the other hand no mixing is possible in osmosis.
- Diffusion cannot be prevented while osmosis can be stopped by applying pressure to the solution.
- Osmosis is possible in liquids only while diffussion can take place in gases as well as liquids.
- In osmosis there is movement from lower concentration to higher concentration but in diffussion, the movement from higher to lower concentration takes place.

Osmotic Pressure

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

Osmotic pressure $(\pi) = hdg$ (approximate)

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

d = density of solution

Laws of Osmotic Pressure

van't Hoff realised that an analogy exists between the gases and solutions provided the osmotic pressure of solutions is used in place of ordinary gas pressure. He showed that for solutions of non-electrolytes the following laws hold good

(i) **Boyle-van't Hoff law** which states that the osmotic pressure (π) of a solution is directly proportional to its concentration (C), when the temperature is kept constant.

$$\pi \propto C \quad \text{(Temperature, } T \text{ is constant)}$$

If V litres of solution contain n moles of solute then

$$C = \frac{n}{V}, \quad \text{or} \quad \pi \propto \frac{1}{V}$$

$$\pi V = \text{constant}$$

Remember The osmotic pressure of a solution containing 1 mole of solute particles per litre (1M) at 0ºC is 22.4 atm.

(ii) **Charles'-van't Hoff law** (Gay-Lussac law) according to which the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T), when the concentration of solution is kept constant.

$$\pi \propto T \quad \text{(Concentration, } C \text{ is constant)}$$

$$\text{or} \qquad \frac{\pi}{T} = \text{constant}$$

(iii) **Avogadro-van't Hoff law** states that equal volumes of dilute solutions of different solutes, having the same temperature and osmotic pressure contain equal number of molecules, i.e. isotonic solutions at a given temperature have same molar concentration.

$$\pi \propto n$$

Here, n = number of moles of solute per litres of solutions.

(iv) **General equation for dilute solutions** is obtained by

$$\pi V = nRT \text{ or } \pi = CRT$$

On the basis of this analogy, van't Hoff proposed that a solute in dissolved state behave as a gas and the osmotic pressure of the solution is equal to the pressure which the solute would exert if it were a gas at the same temperature and occupying the same volume as that of solution.

These laws fail to deal with concentrated solution due to the fact that osmotic pressure is actually related to the activity and not to the concentration of the solution. Osmotic pressure is the most sensitive colligative property and its magnitude is proportional to the molality of the solution.

Determination of Molecular Mass from Osmotic Pressure

$$\therefore \qquad \pi V = nRT$$

$$\Rightarrow \qquad \pi V = \frac{w}{m'} RT$$

$$\text{or} \qquad m' = \frac{wRT}{\pi V}$$

Example 20. *Osmotic pressure of a urea solution at* 10°C *is* 500 mm. *Osmotic pressure of the solution become* 105.3 mm, *when it is diluted and temperature is raised to* 25°C. *The extent of dilution is*

(a) 4 times (b) 3 times
(c) 5 times (d) 2 times

Sol. (c) $\pi V = nRT$

$$\frac{500V_1}{105.3V_2} = \frac{nR \times 283}{nR \times 298}$$

$$\frac{V_1}{V_2} = \frac{1}{5}$$

$$\text{or} \qquad V_2 = 5V_1$$

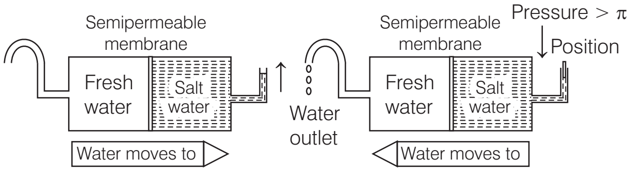
Total Osmotic Pressure

If a number of solutions are present in the solution and $\pi_1, \pi_2, \pi_3, \ldots$ are their individual osmotic pressure then

$$\text{total osmotic pressure, } \pi = \pi_1 + \pi_2 + \pi_3 + \ldots$$

Reverse Osmosis

When a pressure more than the osmotic pressure is applied to the solution, the solvent may pass from solution into the solvent through the semi-permeable membrane. This type of osmosis is known as reverse osmosis. Reverse osmosis is used for the desalination of sea water.



(a) Osmosis (b) Reverse osmosis

A schematic set up for the reverse osmosis used for desalination of sea water

The osmotic pressure of sea water at 15ºC is 25 atm. Isotonic solutions have the same osmotic pressure. If two solutions have different osmotic pressures, the one having lower pressure is called hypotonic and the other with higher pressure is hypertonic solution.

Example 21. *How many gram of glucose must be present in* 0.5 L *of solution for its osmotic pressure to be the same as that of* 9.2 g *of glucose per litre?*

(a) 4.6 g (b) 5.8 g (c) 3.6 g (d) 8.4 g

Sol. (a) For isotonic solution,

$$\frac{w_1}{m_1V_1} = \frac{w_2}{m_2V_2}$$

$$\frac{w_1}{180 \times 0.5} = \frac{9.2}{180 \times 1}$$

or $$w = 4.60 \text{ g}$$

Applications of Osmotic Pressure

Osmotic pressure measurement provided very good method of determination of molecular mass of polymers like proteins etc., due to the following reasons

- Osmotic pressure of a solution containing fewer particles is appreciable and can therefore be measured accurately as compared to ΔT_b or ΔT_f which are very small in these conditions.
- Osmotic pressure is measured at room temperature, hence the method is particularly useful for biomolecules which are generally unstable at higher temperatures.

Osmosis plays a vital role in biology also. Some examples it are as follows

- For normal functioning of the living systems, the fluid concentration has to be maintained in the plant and animal cells.
- Movement of water from roots to the top of plants takes place *via* osmosis.
- Flow of water to various parts of plants is due to osmosis.
- Different movements of plants such as opening and closing of flowers, etc., are controlled by osmosis.
- A 0.91% solution of pure NaCl is isotonic with human red blood red cells (RBCs). Therefore, in this solution, RBCs neither swell nor undergo **plasmolysis**.
- A pure NaCl solution with concentration less than 0.91% is called **hypotonic solution.** On placing RBCs in this solution, these will swell and even burst.
- A pure NaCl solution with concentration more than 0.91% is called **hypertonic solution.** On placing RBCs in this solution, these shink due to plasmolysis.
- People taking a lot of salt or salty food experience water osmosis. The resulting puffiness or swelling is called *edema.*
- The use of salt and sugar as preservatives in pickels and jams has its basis in preventing growth of fungi and bacteria by osmosis.

Abnormal Colligative Properties : van't Hoff Factor

Various relations of colligative properties hold good in dilute solutions only when there is no change in molecular state of solute. In case the total number of particles of solute changes in solution, the colligative properties also change accordingly.

This change occur in the following two ways

By Dissociation

When substance is an electrolyte, the number of particles increases in solution and the colligative property increases accordingly.

In case of dissociation suppose 1 molecule of solute A dissociates to give n ions and α is the degree of dissociation.

	A $\rightleftharpoons$	nB
Initially	1 mol	0
After dissociation	$(1-\alpha)$ mol	$n\alpha$

Total number of moles present in solution

$$= (1-\alpha) + n\alpha = 1 + (n-1)\alpha$$

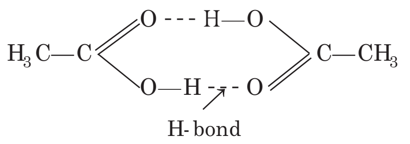
van't Hoff factor, $i = 1 + (n-1)\alpha > 1$ if $n \geq 2$

and $$\alpha = \frac{(i-1)}{(n-1)}$$

By Association

When substance undergoes association, the number of particles decreases in solution and consequently the value of colligative property decreases. Association of molecules is depicted as follows

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$



Molecules of acetic acid dimerise in benzene due to hydrogen bonding. It generally happens in solvents having low dielectric constant.

In case of association suppose n molecules associate to form one giant molecule and α is the degree of association.

	nA $\rightleftharpoons$	$(A)_n$
Initially	1 mol	0
At equilibrium	$(1-\alpha)$ mol	$\frac{\alpha}{n}$

Total number of moles in solution

$$= (1-\alpha) + \frac{\alpha}{n} = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

van't Hoff factor $= 1 + \left(\frac{1}{n} - 1\right)\alpha < 1$ if $n \geq 2$

and $$\alpha = \frac{(i-1)}{\frac{1}{n} - 1}$$

van't Hoff Factor

Normal value of colligative property $\propto$ number of particles of solute taken and abnormal value of colligative property $\propto$ number of particles of solute after dissociation or association.

The ratio of two values, i.e.

$\dfrac{\text{abnormal colligative property}}{\text{normal colligative property}}$ is termed as van't Hoff factor (i).

$$i = \frac{\text{No. of particles after association or dissociation}}{\text{No. of particles before association or dissociation}}$$

Thus, $i = \dfrac{\text{actual number of particles in solution}}{\text{number of particles taken}}$

Abnormal Molecular Weight

$$\text{As, colligative properties } \propto \frac{1}{\text{(molecular weight)}}$$

$$i = \frac{\text{Normal molecular weight}}{\text{Abnormal molecular weight}}$$

$$= 1 + (n-1)\alpha > 1 \text{ in case of dissociation}$$

$$= 1 + \left(\frac{1}{n} - 1\right)\alpha < 1 \text{ in case of association}$$

In case van't Hoff factor is known, the various colligative properties would be given by

$$\Delta T_f = i\, k_f\, m$$

$$\Delta T_b = i\, k_b\, m$$

$$\pi V = inRT$$

$$\frac{p^\circ - p}{p^\circ} = i x_B$$

where, m is the molality of solution, $i \times m$ is sometimes referred to as **effective molality** or **colligative molality** (m_i).

$$\therefore \qquad m_i = i \times m$$

and

$$\Delta T_f = k_f\, m_i$$

$$\Delta T_b = k_b m_i$$

Example 22. *The freezing point depression of* 0.1 *molal solution of acetic acid in benzene is* 0.256 K. k_f *for benzene is* 5.12 K kg mol^{-1}. *What conclusion can you draw about the molecular state of acetic acid in benzene?*

(a) Acetic acid is doubly associated
(b) Benzene is doubly associated
(c) Both are equally associated
(d) None of the above

Sol. (a) $i = \dfrac{\text{observed colligative property}}{\text{calculated colligative property}} = \dfrac{0.256}{0.512} = \dfrac{1}{2}$

Also, $\quad i = \dfrac{\text{calculated molecular mass}}{\text{observed molecular mass}}$

Calculated molecular mass of $CH_3COOH = 60$

$\therefore$ Observed molecular mass $= \dfrac{60}{1/2} = 120$

Hence, acetic acid exists as doubly associated.

Example 23. *Which one of the following aqueous solutions will exhibit highest boiling point?*

(a) 0.01 M Na_2SO_4
(b) 0.01 M KNO_3
(c) 0.015 M urea
(d) 0.015 M glucose

Sol. (a) $\Delta T \propto im$ (as k_f is a constant)

(a) $\Delta T \propto 3 \times 0.01 = 0.03$ (because it gives 3 ions)
(b) $\Delta T \propto 2 \times 0.01 = 0.02$ (because it gives 2 ions)
(c) $\Delta T \propto 0.015 \times 1 = 0.015$ (No ions are obtained)
(d) $\Delta T \propto 0.015 \times 1 = 0.015$

Since, ΔT is highest for 0.01 M Na_2SO_4 so it will exhibit highest boiling point.

Practice Exercise

ROUND I Topically Divided Problems

Type of Solutions, Solubility and their Concentrations

1. A beaker contains a solution of substance '*A*'. Precipitation of substance '*A*' takes place when small amount of '*A*' is added to the solution. The solution is *(NCERT Exemplar)*

(a) saturated (b) supersaturated
(c) unsaturated (d) concentrated

2. Value of Henry's constant K_H *(NCERT Exemplar)*

(a) increases with increase in temperature
(b) decreases with increase in temperature
(c) remains constant
(d) first increases then decreases

3. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to *(NCERT Exemplar)*

(a) low temperature
(b) low atmospheric pressure
(c) high atmospheric pressure
(d) both low temperature and high atmospheric pressure

4. K_H value for Ar (g), $CO_2(g)$, HCHO(g) and $CH_4(g)$ are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility. *(NCERT Exemplar)*

(a) $HCHO < CH_4 < CO_2 < Ar$
(b) $HCHO < CO_2 < CH_4 < Ar$
(c) $Ar < CO_2 < CH_4 < HCHO$
(d) $Ar < CH_4 < CO_2 < HCHO$

5. Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN. *(NCERT)*

(a) 1.40 (b) 1.90 (c) 2.60 (d) 2.29

6. Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mmHg. Calculate the solubility of methane in benzene at 298 K under 760 mmHg. *(NCERT)*

(a) 1.78×10^{-4} (b) 1.78×10^{-3}
(c) 17.8×10^{-4} (d) 1.78×10^{-6}

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

(a) 1.89 g (b) 4.57 g
(c) 2.99 g (d) 3.54 g

8. An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. If the density of the solution is 1.072 g mL^{-1} then what shall be the molarity of the solution? *(NCERT)*

(a) 91 M (b) 9.1 M
(c) 0.91 M (d) 0.0091 M

9. Increasing the temperature of an aqueous solution will cause

(a) decrease in molarity
(b) decrease in molality
(c) decrease in mole fraction
(d) decrease in % w/w

10. 19.85 mL of 0.1 N NaOH reacts with 20 mL of HCl solution for complete neutralisation. The molarity of HCl solution is

(a) 9.9 (b) 0.99 (c) 0.099 (d) 0.0099

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

(a) 4.18 M (b) 1.84 M (c) 8.41 M (d) 18.4 M

12. A 6.50 molal solution of KOH (*aq.*) has a density of 1.89 g cm^{-3}. The molarity of the solution is ……… mol dm^{-3}. *(JEE Main 2021)*

[Atomic masses : K : 39.0 u ; O : 16.0 u ; H: 1.0 u]

(a) 9 (b) 10 (c) 16 (d) 18

13. Calculate the molality of 1 L solution of 93% H_2SO_4 (weight/volume). The density of the solution is 1.84 g/mL.

(a) 11.05 (b) 12.05 (c) 13.05 (d) 10.05

14. Which of the following solutions has the highest normality?

(a) 6 g of NaOH/100 mL (b) 0.5 M H_2SO_4
(c) N phosphoric acid (d) 8 g of KOH/L

15. 100 mL of 0.3 N HCl is mixed with 200 mL of 0.6 N H_2SO_4. The final normality of the resulting solution will be

(a) 0.3 N (b) 0.2 N (c) 0.5 N (d) 0.1 N

16. Based on solute-solvent interactions, arrange the following in the order of increasing solubility in *n*-octane. Cyclohexane, KCl, CH_3OH, CH_3CN. ***(NCERT)***

(a) KCl < CH_3OH < CH_3CN < Cyclohexane
(b) CH_3OH < KCl < CH_3CN < Cyclohexane
(c) CH_3OH < CH_3CN < KCl < Cyclohexane
(d) None of the above

17. Calculate the molarity of solution of $CaCl_2$ if on chemical analysis it is found that 200 mL of $CaCl_2$ contains 3.01×10^{22} Cl^- ions.

(a) 40 M (b) 3.01 M (c) 0.125 M (d) 0.250 M

18. What volume of 12 N and 3 N HCl must be mixed to give 1.00 L of 6.00 N HCl?

(a) 0.33 L, 0.66 L (b) 0.33 L, 0.33 L
(c) 0.66 L, 0.66 L (d) 0.8 L, 0.2 L

19. The volume of water to be added to 100 cm^3 of 0.5 N H_2SO_4 to get decinormal concentration is

(a) 400 cm^3 (b) 500 cm^3 (c) 450 cm^3 (d) 100 cm^3

20. A dry air is passed through the solution, containing the 10 g of solute and 90 g of water and then it is passed through pure water. There is the depression in weight of solution by 2.5 g and in weight of pure solution by 0.05 g. Calculate the molecular weight of solute.

(a) 25 (b) 50 (c) 100 (d) 180

21. Mark the correct relationship between the boiling points of very dilute solutions of $BaCl_2$ (t_1) and KCl (t_2), having the same molarity.

(a) $t_1 = t_2$ (b) $t_1 < t_2$
(c) $t_2 < t_1$ (d) cannot be calculated

22. Match the following:

Column I	Column II
I. Foam	A. Smoke
II. Gel	B. Cell fluid
III. Aerosol	C. Jellies
IV. Emulsion	D. Rubber
	E. Froth
	F. Milk

Codes ***(JEE Main 2020)***

(a) (I)-(D), (II)-(B), (III)-(A), (IV)-(E)
(b) (I)-(B), (II)-(C), (III)-(E), (IV)-(D)
(c) (I)-(E), (II)-(C), (III)-(A), (IV)-(F)
(d) (I)-(D), (II)-(B), (III)-(E), (IV)-(F)

23. A solution of two components containing n_1 moles of the 1st component and n_2 moles of the 2nd component is prepared. M_1 and M_2 are the molecular weights of component 1 and 2 respectively. If d is the density of the solution in g mL^{-1}, C_2 is the molarity and χ_2 is the mole-fraction of the 2nd component, then C_2 can be expressed as ***(JEE Main 2020)***

(a) $C_2 = \dfrac{1000\,\chi_2}{M_1 + \chi_2\,(M_2 - M_1)}$ (b) $C_2 = \dfrac{d\chi_2}{M_2 + \chi_2\,(M_2 - M_1)}$

(c) $C_2 = \dfrac{1000\,d\chi_2}{M_1 + \chi_2\,(M_2 - M_1)}$ (d) $C_2 = \dfrac{d\chi_1}{M_2 + \chi_2\,(M_2 - M_1)}$

24. On litre sample of hard water contains 1 mg of $CaCl_2$ and 1 mg of $MgCl_2$. Find the total hardness of water in terms of $CaCO_3$ per 10^6 parts of water by mass.

(a) 1.753 ppm (b) 1.953 ppm
(c) 1.243 ppm (d) 1.533 ppm

25. 18 g of glucose $(C_6H_{12}O_6)$ is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is ***(JEE Main 2016 (Offline))***

(a) 76.0 (b) 752.4 (c) 759.0 (d) 7.6

Raoult's Law and Vapour Pressure (Ideal and Non-Ideal Solutions)

26. If two liquids A and B form minimum boiling azeotrope at some specific composition then ***(NCERT Exemplar)***

(a) $A — B$ interactions are stronger than those between $A — A$ or $B — B$
(b) vapour pressure of solution increases because more number of molecules of liquids A and B can escape from the solution
(c) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution
(d) $A — B$ interactions are weaker than those between $A — A$ or $B — B$

27. Formation of a solution from two components can be considered as

I. Pure solvent → separated solvent molecules; ΔH_1
II. Pure solute → separated solute molecules; ΔH_2
III. Separated solvent and solute molecules → solution, ΔH_3

Solution so formed will be ideal if

(a) $\Delta H_{sol} = \Delta H_1 - \Delta H_2 - \Delta H_3$
(b) $\Delta H_{sol} = \Delta H_3 - \Delta H_1 - \Delta H_2$
(c) $\Delta H_{sol} = \Delta H_1 + \Delta H_2 + \Delta H_3$
(d) $\Delta H_{sol} = \Delta H_1 + \Delta H_2 - \Delta H_3$

28. When two liquids A and B are mixed then their boiling points becomes greater than both of them. What is the nature of this solution?

(a) Ideal solution
(b) Normal solution
(c) Negative deviation with non-ideal solution
(d) Positive deviation with non-ideal solution

29. For the determination of molecular weights, Raoult's law is applicable only to

(a) dilute solutions of electrolytes
(b) concentrated solutions of electrolytes
(c) dilute solutions of non-electrolytes
(d) concentrated solutions of non-electrolytes

30. Vapour pressure of CCl_4 at 25°C is 143 mm of Hg and 0.5 g of a non-volatile solute (mol. wt. = 65) is dissolved in 100 mL CCl_4. Find the vapour pressure of the solution. (Density of $CCl_4 = 1.58\ g / cm^3$).

(a) 94.39 mm (b) 141.93 mm
(c) 134.44 mm (d) 199.34 mm

31. The vapour pressure of pure liquids A and B are 450 and 700 mmHg respectively, at 350 K. If total vapour pressure is 600 mmHg, find the composition of B in vapour phase. ***(NCERT)***

(a) 0.30 (b) 0.40 (c) 0.60 (d) 0.70

32. 100 g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 torr. ***(NCERT)***

(a) 500, 450 (b) 280, 500
(c) 280, 32 (d) 500, 280

33. Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapour pressures of pure A and pure B are 7×10^3 Pa and 12×10^3 Pa, respectively. The composition of the vapour in equilibrium with a solution containing 40 mole percent of A at this temperature is ***(JEE Main 2019)***

(a) $\chi_A = 0.76; \chi_B = 0.24$ (b) $\chi_A = 0.28; \chi_B = 0.72$
(c) $\chi_A = 0.4; \chi_B = 0.6$ (d) $\chi_A = 0.37; \chi_B = 0.63$

34. Liquid M and liquid N form an ideal solution. The vapour pressures of pure liquids M and N are 450 and 700 mmHg, respectively, at the same temperature. Then correct statement is

x_M = mole fraction of M in solution;
x_N = mole fraction of N in solution;
y_M = mole fraction of M in vapour phase;
y_N = mole fraction of N in vapour phase ***(JEE Main 2019)***

(a) $\frac{x_M}{x_N} > \frac{y_M}{y_N}$ (b) $\frac{x_M}{x_N} = \frac{y_M}{y_N}$
(c) $\frac{x_M}{x_N} < \frac{y_M}{y_N}$ (d) $(x_M - y_M) < (x_N - y_N)$

35. Two open beakers one containing a solvent and the other containing a mixture of that solvent with a non-volatile solute are together sealed in a container. Over time ***(JEE Main 2020)***

(a) the volume of the solution decreases and the volume of the solvent increases
(b) the volume of the solution does not change and the volume of the solvent decreases
(c) the volume of the solution increases and the volume of the solvent decreases
(d) the volume of the solution and the solvent does not change

36. At 35°C, the vapour pressure of CS_2 is 512 mmHg and that of acetone is 344 mmHg. A solution of CS_2 in acetone has a total vapour pressure of 600 mmHg. The false statement amongst the following is ***(JEE Main 2020)***

(a) Raoult's law is not obeyed by this system
(b) CS_2 and acetone are less attracted to each other than to themselves
(c) a mixture of 100 mL CS_2 and 100 mL acetone has a volume < 200 mL
(d) heat must be absorbed in order to produce the solution at 35°C

37. The vapour pressure of two liquid P and Q are 80 and 60 torr respectively. The total vapour pressure of solution obtained by mixing 3 moles of P and 2 moles of Q would be ***(AIIMS 2012)***

(a) 140 torr (b) 20 torr
(c) 68 torr (d) 72 torr

38. At a given temperature, the vapour pressure in mm of Hg of a liquid A and B is given by the equation $p = 120 - 80\ X_B$ (X_B = mole fraction of B)
Vapour pressure of pure A and B at the same temperature are respectively

(a) 120, 80 (b) 120, 200
(c) 120, 40 (d) 80, 40

39. For an ideal solution with $p_A^\circ > p_B^\circ$, which of the following is true?

(a) $(\chi_A)_{\text{liquid}} = (\chi_A)_{\text{vapour}}$
(b) $(\chi_A)_{\text{liquid}} > (\chi_A)_{\text{vapour}}$
(c) $(\chi_A)_{\text{liquid}} < (\chi_A)_{\text{vapour}}$
(d) $(\chi_A)_{\text{liquid}}$ and $(\chi_A)_{\text{vapour}}$ do not bear any relationship with each other.

40. Total vapour pressure of mixture of 1 mole A ($p_A^\circ = 150$ torr) and 2 moles B ($p_B^\circ = 240$ torr) is 200 torr. In this case

(a) there is positive deviation from Raoult's law
(b) there is negative deviation from Raoult's law
(c) there is no deviation from Raoult's law
(d) molecular masses of A and B are also required for calculating the deviation

41. A binary solution of ethanol and n-heptane example of

(a) ideal solution
(b) non-ideal solution with + ve deviation
(c) non-ideal solution with – ve deviation
(d) unpredictable behaviour

42. Negative deviation from Raoult' law is observed in which one of the following binary liquid mixtures?

(a) Ethanol and acetone
(b) Benzene and toluene
(c) Acetone and chloroform
(d) Chloroethane and bromoethane
(e) Acetone and carbon disulphide

43. If ethanol dissolves in water then which of the following would happen?

(a) Absorption of heat and contraction of volume.
(b) Liberation of heat and contraction of volume.
(c) Absorption of heat and increase in volume.
(d) Liberation of heat and increase in volume.

44. Which one of the following binary liquid systems shows positive deviation from Raoult's law?

(a) Benzene-Toluene
(b) Carbon disulphide-acetone
(c) Phenol-aniline
(d) Chloroform-acetone
(e) Nitric acid-water

45. Which will form maximum boiling azeotrope?

(a) $HNO_3 + H_2O$ solution
(b) $C_2H_5OH + H_2O$ solution
(c) $C_6H_6 + C_6H_5CH_3$ solution
(d) None of the above

Colligative Properties

46. Lowering of vapour pressure is highest for

(a) 0.1 M $BaCl_2$
(b) 0.1 M glucose
(c) 0.1 M $MgSO_4$
(d) Urea

47. Which one of the statements given below concerning properties of solutions, describes a colligative effect?

(a) Vapour pressure of pure water decreases by the addition of nitric acid
(b) Boiling point of pure water decreases by the addition of ethanol
(c) Boiling point of pure benzene increases by the addition of toluene
(d) Vapour pressure of pure benzene decreases by the addition of naphthalene

48. The vapour pressure of water at 20°C is 17.54 mm. When 20 g of a non-ionic substance is dissolved in 100 g of water, the vapour pressure is lowered by 0.30 mm. What is the molecular mass of the substance?

(a) 200.8 (b) 206.88
(c) 210.5 (d) 215.2

49. Vapour pressure of water at 293 K is 17.535 mmHg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water. *(NCERT)*

(a) 17.43 mmHg (b) 18.93 mmHg
(c) 20.12 mmHg (d) 25.31 mmHg

50. The unit of ebullioscopic constant is *(NCERT Exemplar)*

(a) $K\ kg\ mol^{-1}$ or $K\ (molality)^{-1}$
(b) $mol\ kg\ K^{-1}$ or $K^{-1}\ (molality)$
(c) $kg\ mol^{-1}\ K^{-1}$ or $K^{-1}\ (molality)^{-1}$
(d) $K\ mol\ kg^{-1}$ or $K\ (molality)$

51. The molar freezing point constant for water is $1.86°\ C\ mol^{-1}$. If 342 g of cane sugar ($C_{12}H_{22}O_{11}$) is dissolved in 1000 g of water, the solution will freeze at

(a) −1.86° C (b) −2.86° C (c) +1.86°C (d) +2.86°C

52. The amount of ice that will separate out on cooling a solute containing 50 g of ethylene glycol in 200 g water to –9.3°C will be ($K_f = 1.86\ K\ kg\ mol^{-1}$)

(a) 8.37 g (b) 161.3 g (c) 3.87 g (d) 38.7 g

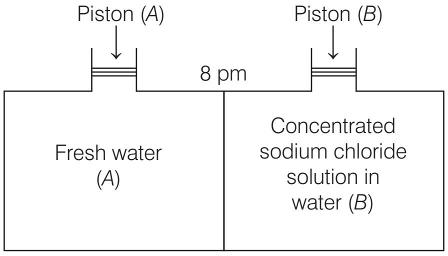
53. The molecular weight of NaCl determined by studying freezing point depression of its 0.5% aqueous solution is 30. The apparent degree of dissociation of NaCl is

(a) 0.60 (b) 0.50 (c) 0.30 (d) 0.95

54. Which of the following statements is false? *(NCERT Exemplar)*

(a) Units of atmospheric pressure and osmotic pressure are the same
(b) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration
(c) The value of molal depression constant depends on nature of solvent
(d) Relative lowering of vapour pressure is a dimensionless quantity

55. Consider the figure and mark the correct option.



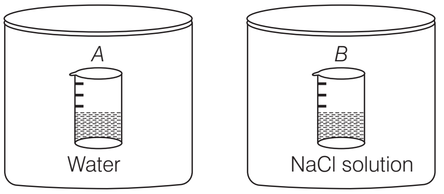
(NCERT Exemplar)

(a) Water will move from side (A) to side (B) if a pressure lower than osmotic pressure is applied on piston (B)
(b) water will move from side (B) to side (A) if a pressure greater than osmotic pressure is applied on piston (B)
(c) Water will move from side (B) to side (A) if a pressure equal to osmotic pressure is applied on piston (B)
(d) Water will move from side (A) to side (B) if pressure equal to osmotic pressure is applied on piston (A)

56. An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because

(a) it gains water due to osmosis ***(NCERT Exemplar)***
(b) it loses water due to reverse osmosis
(c) it gains water due to reverse osmosis
(d) it loses water due to osmosis

57. Two beakers of capacity 500 mL were taken. One of these beakers, labelled as "A", was filled with 400 mL water whereas the beaker labelled "B" was filled with 400 mL of 2 M solution of NaCl. At the same temperature both the beakers were placed in closed containers of same material and same capacity as shown in the figure. ***(NCERT Exemplar)***



At a given temperature, which of the following statement is correct about the vapour pressure of pure water and that of NaCl solution.

(a) Vapour pressure in container (A) is more than that in container (B)
(b) Vapour pressure in container (A) is less than that in container (B)
(c) Vapour pressure is equal in both the containers
(d) Vapour pressure in container (B) is twice the vapour pressure in container (A)

58. The relationship between osmotic pressure at 273 K when 10 g glucose (p_1), 10 g urea (p_2) and 10 g sucrose (p_3) are dissolved in 250 mL of water is

(a) $p_1 > p_2 > p_3$ (b) $p_3 > p_2 > p_1$
(c) $p_2 > p_1 > p_3$ (d) $p_2 > p_3 > p_1$

59. A 6% solution of urea is isotonic with

(a) 1 M solution of glucose
(b) 0.05 M solution of glucose
(c) 6% solution of glucose
(d) 25% solution of glucose

60. The osmotic pressure of a 5% (wt./vol) solution of cane sugar at 150°C is

(a) 3.078 atm (b) 4.078 atm
(c) 5.078 atm (d) 2.45 atm

61. A 5% solution of sugar cane (mol. wt. = 342) is isotonic with 1% solution of X under similar conditions. The molecular weight of X is

(a) 136.2 (b) 68.4
(c) 34.2 (d) 171.2

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

(a) 0.02 (b) 0.04 (c) 0.08 (d) 0.06

63. Which of the following units is useful in relating concentration of solution with its vapour pressure? ***(NCERT Exemplar)***

(a) Mole fraction (b) Parts per million
(c) Mass percentage (d) Molality

64. 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 kg mol^{-1} and molar mass of ethylene glycol = 62 g mol^{-1}) ***(AIEEE 2011)***

(a) 804.32 g (b) 204.30 g
(c) 400.00 g (c) 304.60 g

65. A solution of urea in water has a boiling point of 100.128°C. Find the freezing point of the same solution. Molal constants of water k_f and k_b are 1.86°C and 0.512°C respectively.

(a) − 0.346°C (b) − 0.465°C
(c) + 0.465°C (d) − 0.256°C

66. What is the freezing point of a 10% (by weight) solution of CH_3OH in water?

(a) 90°C (b) 10°C
(c) 6.45°C (d) − 6.45°C

67. Two elements A and B form compounds having formulae AB_2 and AB_4. When dissolved in 20 g benzene, 1 g of AB_2 lowers the freezing point by 2.3° whereas 1.0 g of AB_4 lowers it by 1.3°C. K_f for benzene is 5.1 K mol^{-1} kg. The atomic masses of A and B are respectively

(a) 25.6, 42.6 (b) 42.6, 25.6
(c) 85.3, 25.6 (d) 25.6, 85.3

68. The freezing point of a 0.01 M aqueous glucose solution at 1 atmosphere is – 0.18°C. To it, an addition of equal volume of 0.002 M glucose solution will; produce a solution with freezing point of nearly

(a) – 0.036°C (b) – 0.108°C
(c) – 0.216°C (d) – 0.22°C

69. In 100 g of naphthalene, 2.423 g of S was dissolved. Melting point of naphthalene = 80.1°C. $\Delta T_f = 0.661$°C. $L_f = 35.7$ cal/g of naphthalene. Molecular formula of sulphur added is

(a) S_2 (b) S_4 (c) S_6 (d) S_8

Abnormal Colligative Properties and van't Hoff Factor

70. We have three aqueous solutions of NaCl labelled as '*A*', '*B*' and '*C*' with concentrations 0.1 M, 0.01 M and 0.001 M, respectively. The value of van't Hoff factor for these solutions will be in the order *(NCERT Exemplar)*

(a) $i_A < i_B < i_C$ (b) $i_A > i_B > i_C$
(c) $i_A = i_B = i_C$ (d) $i_A < i_B > i_C$

71. Which of the following aqueous solutions should have the highest boiling point? *(NCERT Exemplar)*

(a) 1.0 M NaOH (b) 1.0 M Na_2SO_4
(c) 1.0 M NH_4NO_3 (d) 1.0 M KNO_3

72. Which has minimum osmotic pressure?

(a) 200 mL of 2 M NaCl solution
(b) 200 mL of 1 M glucose solution
(c) 200 mL of 2 M urea solution
(d) All have same osmotic pressure

73. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (K_f = 1.72 K kg mol^{-1}), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is

(a) 0.5 (b) 1 (c) 2 (d) 13

74. The freezing point depression of 0.001 m, $K_x[Fe(CN)_6]$ is 7.10×10^{-3} K. If for water, K_f is 1.86 K kg mol^{-1}, value of x will be

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

75. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water using the following information will be (molecular weight of $CuCl_2$ = 134.4 and K_b = 0.52 K $molal^{-1}$)

(a) 0.16 (b) 0.05 (c) 0.1 (d) 0.2

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

(a) –0.35°C (b) –1.35°C
(c) –2.35°C (d) –3.53°C

77. Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 L of water such that its osmotic pressure is 0.75 atm at 27°C. *(NCERT)*

(a) 1.82 g (b) 3.42 g
(c) 2.98 g (d) 1.45 g

78. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 L of water at 25°C, assuming that it is completely dissociated. *(NCERT)*

(a) 2.39×10^{-2} atm (b) 4.29×10^{-3} atm
(c) 5.27×10^{-3} atm (d) 1.39×10^{-4} atm

79. 19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the degree of dissociation and dissociation constant of fluoroacetic acid. K_f = 1.86 K kg mol^{-1} *(NCERT)*

(a) 0.07 and 3.07×10^{-3} (b) 0.04 and 3.07×10^{-3}
(c) 0.082 and 4.23×10^{-4} (d) 0.07 and 4.23×10^{-4}

80. A 1% (w/V) KCl solution is ionised to the extent of 82%. What would be its osmotic pressure at 291 K? (R = 0.083 L bar K^{-1} mol^{-1})

(a) 1.82 bar (b) 5.9 bar
(c) 82 bar (d) 100 bar

81. The osmotic pressure of a dilute solution of an ionic compound XY in water is four times that of a solution of 0.01 M $BaCl_2$ in water. Assuming complete dissociation of the given ionic compounds in water, the concentration of XY (in mol L^{-1}) in solution is *(JEE Main 2019)*

(a) 4×10^{-2} (b) 16×10^{-4}
(c) 4×10^{-4} (d) 6×10^{-2}

82. Calculate osmotic pressure of a solution obtained by mixing 100 mL of 3.4% (mass/vol.) solution of urea (molar mass 60) and 100 mL of 1.6 % solution of cane-sugar (molar mass 342) at 20°C.

(a) 6.38 atm (b) 7.38 atm
(c) 4.33 atm (d) 8.38 atm

83. Elevation in the boiling point for 1 molal solution of glucose is 2 K. The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K. The relation between K_b and K_f is **(JEE Main 2019)**

(a) $K_b = 1.5\ K_f$ (b) $K_b = 0.5\ K_f$
(c) $K_b = K_f$ (d) $K_b = 2K_f$

84. The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be (K_f for benzene = 5.12 K kg mol^{-1})

(a) 64.6 % (b) 80.4 % (c) 74.6 % (d) 94.6 %

85. A solution contain 62 g of ethylene glycol in 250 g of water is cooled upto –10°C. If K_f for water is 1.86 K kg mol^{-1}, then amount of water (in g) separated as ice is *(JEE Main 2019)*

(a) 32 (b) 48 (c) 64 (d) 16

86. Molal depression constant for a solvent is 4.0 K kg mol^{-1}. The depression in the freezing point of the solvent for 0.03 mol kg^{-1} solution of K_2SO_4 is

(Assume complete dissociation of the electrolyte) *(JEE Main 2019)*

(a) 0.18 K (b) 0.36 K (c) 0.12 K (d) 0.24 K

87. At room temperature, a dilute solution of urea is prepared by dissolving 0.60 g of urea in 360 g of water. If the vapour pressure of pure water at this temperature is 35 mmHg, lowering of vapour pressure will be (Molar mass of urea = 60 g mol^{-1}) *(JEE Main 2019)*

(a) 0.027 mmHg (b) 0.031 mmHg
(c) 0.017 mmHg (d) 0.028 mmHg

88. 1 g of a non-volatile, non-electrolyte solute is dissolved in 100 g of two different solvents A and B, whose ebullisocopic constants are in the ratio of 1 : 5. The ratio of the elevation in their boiling points, $\frac{\Delta T_b(A)}{\Delta T_b(B)}$, is *(JEE Main 2019)*

(a) 5 : 1 (b) 10 : 1
(c) 1 : 5 (d) 1 : 0.2

89. The freezing point of a diluted milk sample is found to be –0.2°C, while it should have been –0.5°C for pure milk. How much water has been added to pure milk to make the diluted sample? *(JEE Main 2019)*

(a) 2 cups of water to 3 cups of pure milk
(b) 1 cup of water to 3 cups of pure milk
(c) 3 cups of water to 2 cups of pure milk
(d) 1 cup of water to 2 cups of pure milk

90. K_2HgI_4 is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is *(JEE Main 2019)*

(a) 1.6 (b) 1.8
(c) 2.2 (d) 2.0

91. Molecules of benzoic acid (C_6H_5COOH) dimerise in benzene. 'w' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2 K. If the percentage association of the acid to form dimer in the solution is 80, then w is (Given that $K_f = 5$ K kg mol^{-1}, molar mass of benzoic acid = 122 g mol^{-1}) *(JEE Main 2019)*

(a) 1.8 g (b) 1.0 g
(c) 2.4 g (d) 1.5 g

ROUND II Mixed Bag

1. The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% and 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K if the Henry's law constants for oxygen and nitrogen at 298 K are 3.30×10^7 mm and 6.51×10^7 mm respectively, the composition of O_2 and N_2 gases in water respectively are *(NCERT)*

(a) $4.6\times 10^{-5}, 9.22\times 10^{-5}$
(b) $9.22\times 10^{-5}, 4.6\times 10^{-5}$
(c) $4.6\times 10^{-5}, 4.12\times 10^{-5}$
(d) $4.12\times 10^{-5}, 4.6\times 10^{-5}$

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

(a) 2.82 g (b) 1.85 g
(c) 9.62 g (d) 11.2 g

3. Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of 1.5×10^{-3} m aqueous solution required for the above dose. *(NCERT)*

(a) 3.2×10^{-2} kg (b) 3.2×10^{-4} kg
(c) 3.2×10^{-3} kg (d) 3.2×10^{-5} kg

4. On the basis of information given below mark the correct option. Information

A. In bromoethane and chloroethane mixture intermolecular interactions of *A*—*A* and *B*—*B* type are nearly same as *A*—*B* type interactions.

B. In ethanol and acetone mixture *A*—*A* or *B*—*B* type intermolecular interactions are stronger than *A*—*B* type interactions.

C. In chloroform and acetone mixture *A*—*A* or *B*—*B* type intermolecular interactions are weaker than *A*—*B* type interactions.

(NCERT Exemplar)

(a) Solution (*B*) and (*C*) will follow Raoult's law
(b) Solution (*A*) will follow Raoult's law
(c) Solution (*B*) will show negative deviation from Raoult's law
(d) Solution (*C*) will show positive deviation from Raoult's law

5. When mercuric iodide is added to the aqueous solution of potassium iodide, the
(a) freezing point is raised
(b) freezing point is lowered
(c) freezing point does not change
(d) boiling point does not change

6. Which of the following aqueous solutions produce the same osmotic pressure?
(i) 0.1 M NaCl solution
(ii) 0.1 M glucose solution
(iii) 0.6 g urea in 100 mL solution
(iv) 1.0 g of a non-electrolyte solute (X) in 50 mL solution (molar mass of $X = 200$)
(a) (i), (ii), (iii)
(b) (ii), (iii), (iv)
(c) (i), (ii), (iv)
(d) (i), (iii), (iv)

7. A 0.025 M solution of monobasic acid had a freezing point of –0.060°C. The pK_a for the acid is ($K_b = 1.86$ K kg mol^{-1})
(a) 1.2 (b) 2 (c) 2.5 (d) 5.7

8. How many gram of sucrose (mol. wt. = 342) should be dissolved in 100 g water in order to produce a solution with a 105.0°C difference between the freezing point and boiling temperature?
($K_f = 1.860°\text{C / m}, K_b = 0.151°\text{C/m}$)
(a) 34.2 g (b) 72 g
(c) 342 g (d) 460 g

9. A 5% solution (by mass) of cane sugar in water has freezing point 271 K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K. ***[NCERT]***
(a) 250 K (b) 269 K
(c) 310 K (d) 275 K

10. Benzene and naphthalene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and naphthalene at 300 K are 50.71 mmHg and 32.06 mmHg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of naphthalene. ***(NCERT)***
(a) 0.67 (b) 0.32 (c) 0.85 (d) 0.42

11. A certain substance '*A*' tetramerises in water to the extent of 80%. A solution of 2.5 g of *A* in 100 g of water lowers the freezing point by 0.3°C. The molar mass of *A* is
(a) 31 (b) 62 (c) 122 (d) 244

12. Two solutions of glucose have osmotic pressure 1.0 and 3.5 atm. If 1 L of first solution is mixed with *V* L of second solution, the osmotic pressure of the resultant solution becomes 2.5 atm. Volume of second solution is
(a) 1.0 L (b) 1.5 L (c) 2.5 L (d) 3.5 L

13. A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate the vapour pressure of water at 298 K. ***(NCERT)***
(a) 3.5 kPa (b) 8.2 kPa
(c) 4.2 kPa (d) 1.9 kPa

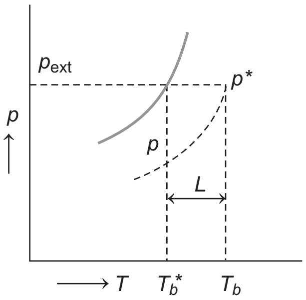
14. Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$; $K_f = 1.86$ K kg mol^{-1}. ***(NCERT)***
(a) 0.42 K (b) 0.82 K
(c) 0.19 K (d) 0.65 K

15. Given,

	A	*B*
1.	0.1 M KCl	0.2 M KCl
2.	0.1% (m/V) NaCl	10% (m/V) NaCl
3.	18 gL^{-1} glucose	34.2 gL^{-1} sucrose
4.	20% (m/V) glucose	10% (m/V) glucose

Indicate the number of solutions which is/are isotonic
(a) 1 only (b) 3 only
(c) 4 only (d) 2 only

16. The phase diagram for the pure solvent and solution are recorded below. The quantity indicated by L in the figure is



(a) Δp (b) $K_b \cdot m$ (c) $K_f m$ (d) m

17. 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

(a) 0.50 (b) 0.93 (c) 0.6 (d) 0.27

18. At certain hill-station, pure water boils at 99.725°C. If K_b for water is 0.513°C kg mol^{-1}, the boiling point of 0.69 m solution of urea will be

(a) 100.359°C (b) 103°C

(c) 100.073°C (d) unpredictable

19. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity of this solution is *(AIEEE 2012)*

(a) 0.50 M (b) 1.78 M

(c) 1.02 M (d) 2.05 M

20. K_f water is 1.86 K kg mol^{-1}. If your automobiles 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? *(AIEEE 2012)*

(a) 72 g (b) 93 g (c) 39 g (d) 27 g

21. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH, is supplied. What is the mole fraction of methyl alcohol in the solution ? *[AIEEE 2011]*

(a) 0.100 (b) 0.190 (c) 0.086 (d) 0.050

22. Match the following columns.

	Column I		Column II
A.	10.6 g Na_2CO_3 dissolved in 100 mL solution (density = 1.06 g mL^{-1})	p.	0.1 M
B.	34.2 g L^{-1} sucrose solution (density = 1.0342 g mL^{-1})	q.	1 M
C.	9.8% H_2SO_4 solution (density 1.25 g mL^{-1}	r.	1.25 M
D.	20% aqueous ethanol solution by volume (density = 0.938 g mL^{-1})	s.	3.0 M

Codes

(a) A-p, B-q, C-r, D-s
(b) A-q, B-p, C-s, D-r
(c) A-q, B-r, C-p, D-s
(d) A-q, B-p, C-r, D-s

23. The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression *(AIEEE 2011)*

(a) $\alpha = \dfrac{i-1}{(x+y-1)}$ (b) $\alpha = \dfrac{i-1}{x+y+1}$

(c) $\alpha = \dfrac{x+y-1}{i-1}$ (d) $\alpha = \dfrac{x+y+1}{i-1}$

24. 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 is *(AIEEE 2011)*

(a) 136.2 (b) 171.2

(c) 68.4 (d) 34.2

25. 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 kg mol^{-1} and molar mass of ethylene glycol = 62 g mol^{-1})

(a) 804.32 g (b) 204.30 g *(AIEEE 2011)*

(c) 400.00 g (d) 304.60 g

26. Match the following columns.

Column I (Salt)			Column II (Nature of solubility curve, i.e. solubility vs temperature)
A.	NH_4NO_3	p.	Increases continuously
B.	Li_2CO_3	q.	First increases and then decreases
C.	$Na_2SO_4 \cdot 10H_2O$	r.	Increases but not continuously.
D.	KCl	s.	Decreases continuously.

Codes

(a) A-r, B-q, C-s, D-p
(b) A-p, B-s, C-q, D-r
(c) A-s, B-r, C-q, D-p
(d) A-r, B-s, C-q, D-p

Numeric Value Questions

27. Compound $PdCl_4.6H_2O$ is a hydrated complex; 1 m aqueous solution of it has freezing point. 269.28 K. Assuming 100% ionisation of complex, the number of ions furnished by complex in the solution ……… .

28. The osmotic pressure of urea solution at 10°C is 200 mm becomes 105.3 mm when it is diluted and temperature raised to 25°C. The extent of dilution is ……… .

29. The osmotic pressure of a solution containing 40 g of solute (molecular mass 246) per litre at 27°C is ($R = 0.0822$ atm L mol^{-1}) ……… .

30. 12.2 g of benzoic acid ($Mw = 122$) in 100 g water had elevation in boiling point of 0.27. $K_b = 0.54$ K kg mol^{-1}. If there is 100% polymerisation, the number of molecules of benzoic acid in associated state is ……… .

31. The hardness of a water sample containing 10^{-3} M $MgSO_4$ expressed as $CaCO_3$ equivalents (in ppm) is ……

32. The osmotic pressure of a solution of NaCl is 0.10 atm and that of a glucose solution is 0.20 atm. The osmotic pressure of a solution formed by mixing 1 L of the sodium chloride solution with 2 L of the glucose solution is $x \times 10^{-3}$ atm. x is ……… (nearest integer). *(JEE Main 2020)*

33. 10.0 mL of Na_2CO_3 solution is titrated against 0.2 M HCl solution. The following titre values were obtained in 5 readings.

4.8 mL, 4.9 mL, 5.0 mL, 5.0 mL and 5.0 mL.

Based on these readings, and convention of titrimetric estimation of concentration of Na_2CO_3 solution is ……… mM. *(JEE Main 2021)*

Answers

Round I

1. (b)	2. (a)	3. (b)	4. (c)	5. (a)	6. (b)	7. (b)	8. (b)	9. (a)	10. (c)
11. (d)	12. (a)	13. (d)	14. (a)	15. (c)	16. (a)	17. (c)	18. (a)	19. (a)	20. (c)
21. (c)	22. (c)	23. (c)	24. (b)	25. (b)	26. (d)	27. (c)	28. (c)	29. (c)	30. (b)
31. (d)	32. (c)	33. (b)	34. (a)	35. (c)	36. (c)	37. (d)	38. (c)	39. (c)	40. (b)
41. (b)	42. (c)	43. (c)	44. (b)	45. (a)	46. (a)	47. (a)	48. (c)	49. (a)	50. (a)
51. (a)	52. (d)	53. (d)	54. (b)	55. (a)	56. (d)	57. (a)	58. (c)	59. (a)	60. (c)
61. (b)	62. (d)	63. (a)	64. (a)	65. (b)	66. (d)	67. (a)	68. (b)	69. (d)	70. (c)
71. (b)	72. (b)	73. (a)	74. (b)	75. (a)	76. (d)	77. (b)	78. (c)	79. (a)	80. (b)
81. (d)	82. (b)	83. (d)	84. (d)	85. (c)	86. (b)	87. (c)	88. (c)	89. (c)	90. (b)
91. (c)									

Round II

1. (a)	2. (b)	3. (c)	4. (b)	5. (b)	6. (b)	7. (c)	8. (b)	9. (b)	10. (a)
11. (b)	12. (b)	13. (a)	14. (d)	15. (b)	16. (b)	17. (d)	18. (c)	19. (d)	20. (b)
21. (c)	22. (a)	23. (a)	24. (c)	25. (a)	26. (d)	27. (2)	28. (2)	29. (4)	30. (2)
31. (100)	32. (167)	33. (50)							

Solutions

Round I

1. Precipitation occurs when the solution is supersaturated.

3. At high altitudes, atmospheric pressure is low and solubility of gases varies directly with pressure thus, decreases at high altitudes.

This is the reason for low concentration of oxygen in blood and tissues of people living at high altitude.

4. The order of increasing solubility are

$$\text{Ar} < \text{CO}_2 < \text{CH}_4 < \text{HCHO}$$

(As solubility increases as the values of K_{H} decreases)

5. Mass of aspirin $= 6.5$ g

Mass of acetonitrile $= 450$ g

Mass of solution $= (6.5 + 450)\ \text{g} = 456.5$ g

$$\text{Mass }\% = \frac{(6.5\ \text{g})}{(456.5\ \text{g})} \times 100 = 1.424\%$$

6. $K_{\text{H}} = 4.27 \times 10^5$ mmHg (at 298 K), $p = 760$ mm

Applying Henry's law,

$p = K_{\text{H}}\,\chi$ (χ = Mole fraction or solubility of methane)

$$x = \frac{p}{K_{\text{H}}} = \frac{(760\ \text{mm})}{(4.27 \times 10^5\ \text{mm})} = 178 \times 10^{-5} = 1.78 \times 10^{-3}$$

7. Molarity $= 0.15$ M or $0.15\ \text{mol L}^{-1}$

Volume of solution $= 250\ \text{mL} = 0.25$ L

Molar mass of solute

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

$$\text{Molarity} = \frac{\text{mass}}{\text{molar mass}} \times \frac{1}{\text{volume (L)}};$$

$$(0.15\ \text{mol L}^{-1}) = \frac{W}{(122\ \text{g mol}^{-1})} \times \frac{1}{(0.25\ \text{L})}$$

$$\underset{\text{(Benzoic acid)}}{\text{Mass of solute}} = (0.15 \times 122 \times 0.25)\ \text{g} = 4.575\ \text{g}$$

8. Density of the solution $= 1.072\ \text{g mL}^{-1}$

Mass of solution = Mass of solute + Mass of solution

$$= 222.6\ \text{g} + 200\ \text{g} = 422.6\ \text{g}$$

$$\text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{422.6\ \text{g}}{1.072\ \text{g mL}^{-1}} = 394.2\ \text{m L}$$
$$= 0.3942\ \text{L}$$

$$\text{Molarity } (M) = \frac{\text{mass of ethylene glycol / molar mass}}{\text{volume in litres}}$$

$$= \frac{(222.6\ \text{g}) / (62\ \text{g mol}^{-1})}{0.3942\ \text{L}}$$

$$= 9.10\ \text{mol L}^{-1} = 9.10\ \text{M}$$

9. An increases in temperature increase the volume of the solution and thus, decreases its molarity.

10. $$\text{Molarity of base} = \frac{\text{normality}}{\text{acidity}} = \frac{0.1}{1} = 0.1$$

$$M_1V_1 = M_2V_2$$
$$0.1 \times 19.85 = M_2 \times 20$$
$$M_2 = 0.09925 \approx 0.099$$

11. Molarity

$$= \frac{\text{weight \% of solute} \times \text{density of the solution} \times 10}{\text{molecular weight of the solution}}$$

$$= \frac{98 \times 1.84 \times 10}{98} = 18.4$$

12. 6.5 molal KOH = 1000 g solvent has 6.5 moles KOH

so, wt. of solute $= 6.5 \times 56 = 364$ g

wt. of solution $= 1000 + 364 = 1364$

$$\text{Volume of solution} = \frac{1364}{1.89}\ \text{mL}$$

$$\text{Molarity} = \frac{\text{Mole of solution}}{\text{V}_{\text{solution}}\ \text{in Litre}} = \frac{6.5 \times 1.89 \times 1000}{1364} = 9.00$$

14. (a) 6 g of NaOH/100 mL

$$N = \frac{6 \times 1000}{40 \times 100} = 1.5\ \text{N}$$

(b) 0.5 M H_2SO_4

$$N = M \times \text{basicity} = 0.5 \times 2 = 1.0$$

(c) N phosphoric acid, normality = 1

(d) 8 g of KOH/L

$$\text{Normality} = \frac{\text{strength in g / L}}{\text{equivalent weight}} = \frac{8}{56} = 0.14\ \text{N}$$

15. $$N_1V_1 + N_2V_2 = N_3V_3$$
$$0.3 \times 100 + 0.6 \times 200 = N_3 \times 300$$
$$0.3 + 1.2 = 3\text{N}_3$$
$$N_3 = 0.5$$

16. (i) Cyclohexane and n-octane both are non-polar. So, they mix completely in all proportions.

(ii) KCl is an ionic compound, but n-octane is non-polar. So, KCl does not dissolve in n-octane.

(iii) CH_3OH and CH_3CN both are polar but CH_3CN is less polar than CH_3OH. As the solvent is non-polar, CH_3CN will dissolve more than CH_3OH in n-octane.

Order of solubility is

$$\text{KCl} < \text{CH}_3\text{OH} < \text{CH}_3\text{CN} < \text{cyclohexane}.$$

17. $$\underset{1\ \text{mol}}{\text{CaCl}_2} \longrightarrow \text{Ca}^{2+} + \underset{2 \times 6.023 \times 10^{23}\ \text{ions}}{2\text{Cl}^-}$$

$2 \times 6.023 \times 10^{23}$ Cl^- ions are present in = 1 mole of CaCl_2

$$3.01 \times 10^{22}\ \text{Cl}^- \text{ ions are present in } \frac{1 \times 3.01 \times 10^{22}}{2 \times 6.02 \times 10^{23}}$$
$$= 0.025 \text{ mole of CaCl}_2$$

$$M = \frac{\text{number of moles}}{\text{volume of solution (in L)}}$$

$$= \frac{0.025}{200} \times 1000 = 0.125 \text{ M}$$

18. L-equivalents of solution

$$= 1\text{ L} \times \left(\frac{6.00 \text{ eq.}}{\text{L}}\right) = 6.00 \text{ eq}$$

Let $\quad x$ = volume of concentrated solution. Then

$1.00 - x$ = volume of dilute solution

$$(x)\left(\frac{12.0 \text{ eq}}{\text{L}}\right) + (1.00 - x)\left(\frac{3.00 \text{ eq}}{\text{L}}\right) = 6.00 \text{ eq}$$

On solving, $x = 0.333$

$\therefore$ Volume of concentrated solution = 0.33 L

and, Volume of dilute solution = 1 – 0.33 = 0.67 L

19. Let the total volume of solution = x

$$\therefore \quad V_2 = \frac{N_1V_1}{N_2} = \frac{0.5 \times 100}{0.1} = 500 \text{ cm}^3$$

$\therefore$ The volume of water added = $500 - 100 \text{ cm}^3 = 400 \text{ cm}^3$

20. $\because$ Lowering in weight of solution $\propto$ solution pressure (p_s)

and lowering in weight of solvent $\propto p^\circ - p_s$

($\because$ p° = vapour pressure of pure solvent)

$$\text{Thus,} \quad \frac{p^\circ - p_s}{p_s} = \frac{\text{lowering in weight of solvent}}{\text{lowering in weight of solution}} = \frac{0.05}{2.5}$$

But according to Raoult's law,

$$\frac{p^\circ - p_s}{p_s} = \frac{w}{m} \times \frac{M}{W}$$

$$\therefore \quad \frac{0.05}{2.5} = \frac{10 \times 18}{90 \times m} \quad \Rightarrow \quad m = \frac{10 \times 18 \times 2.5}{90 \times 0.05} = 100 \text{ g mol}^{-1}$$

21. $BaCl_2$ furnishes more ions than KCl and thus, shows higher boiling point, i.e. $t_1 > t_2$.

22. Correct match is (I) → E, (II) → C, (III) → A, (IV) → F

(I) Foam – Froth

Foam forms gas particles trapped in solid or liquid.

(II) Gel – Jellies

Gel is a colloid, where dispersed phase is liquid and dispersion medium is solid.

(III) Aerosol – Smoke

Aerosol is a colloid, where solid/liquid particles dispersed in gas.

(IV) Emulsion– Milk

Emulsion is formed by mixing two liquids. (Milk is combination of 2 liquid)

23. In first component,

Mass = number of moles × molecular weight = n_1M_1

In second component, Mass = n_2M_2

Mass of solution = $n_1M_1 + n_2M_2$ ...(i)

$$\text{Mole-fraction } (\chi_2) = \frac{n_2}{n_1 + n_2}$$

$$\therefore \quad n_1 = \frac{n_2(1 - \chi_2)}{\chi_2} \qquad \text{...(ii)}$$

Place the value of n_1 in eq. (i)

$$\therefore \quad \frac{n_2(1 - \chi_2)M_1}{\chi_2} + n_2M_2$$

$$\Rightarrow \quad \frac{n_2}{\chi_2}(M_2\chi_2 - M_1\chi_2 + M_1)$$

Volume of solution,

$$= \frac{n_2(M_2\chi_2 - M_1\chi_2 + M_1)}{1000 \times d \times \chi_2} \text{L}$$

$$C_2 = \frac{1000 \times n_2 \times d\chi_2}{n_2(M_2\chi_2 - M_1\chi_2 + M_1)}$$

$$\therefore \quad C_2 = \frac{1000d\,\chi_2}{M_1 + \chi_2(M_2 - M_1)}$$

Hence, the correct option is (c).

24. m M of $MgCl_2$

$$= \frac{1 \times 10^{-3} \times 10^3}{95} = \frac{1}{95}\left(\text{milli mole} = \frac{\text{mass}}{\text{M. mass}} \times 1000\right)$$

$$\text{m M } CaCl_2 = \frac{1 \times 10^{-3} \times 10^3}{111} = \frac{1}{111}$$

$\therefore$ m M of $CaCl_2$, if $MgCl_2$ and $CaCl_2$ are taken in form of $CaCO_3$.

$$= \frac{1}{95} + \frac{1}{111} = \frac{206}{111 \times 95}$$

($\because$ Ca, Mg both are bivalent, $\therefore$ mole ratio is 1 : 1)

$$1000 \text{ mL water has } CaCO_3 = \frac{206 \times 100}{111 \times 95 \times 1000}$$

$\therefore$ 10^6 mL water has $CaCO_3$

$$= \frac{206 \times 100 \times 10^6}{111 \times 95 \times 1000 \times 1000} = 1.953$$

$\therefore \qquad$ Hardness = 1.953 ppm.

25. Vapour pressure of water (p°) = 760 torr

$$\text{Number of moles of glucose} = \frac{\text{mass } (g)}{\text{molecular mass } (g \text{ mol}^{-1})}$$

$$= \frac{18 \text{ g}}{180 \text{ g mol}^{-1}} = 0.1 \text{ mol}$$

Molar mass of water = 18 g/mol

Mass of water (given) = 178.2 g

Number of moles of water

$$= \frac{\text{mass of water}}{\text{molar mass of water}} = \frac{178.2\text{g}}{18 \text{ g/mol}} = 9.9 \text{ mol}$$

Total number of moles = (0.1 + 9.9) mol = 10 mol

Now, mole fraction of glucose in solution = Change in pressure with respect to initial pressure

$$\text{i.e.} \quad \frac{\Delta p}{p^\circ} = \frac{0.1}{10}$$

$$\text{or} \quad \Delta p = 0.01p^\circ = 0.01 \times 760 = 7.6 \text{ torr}$$

$\therefore$ Vapour pressure of solution = (760 – 7.6) = 752.4 torr

26. If two liquids A and B form minimum boiling azeotrope at some specific composition then A — B interactions are weaker than those between A— A or B—B.

28. The one whose boiling point is more than that of either of the two pure components is known as azeotropic mixture with maximum boiling point. This is formed by non-ideal solutions showing negative deviation.

30. Relative lowering in vapour pressure,

$$\frac{p^\circ - p_s}{p^\circ} = \frac{w \times M}{m \times W}$$

$$\frac{143 - p_s}{143} = \frac{0.5}{65} \times \frac{154}{1.58 \times 100}$$

[∵ molecular weight of CCl_4 = 154 and weight = density × volume]

$$143 - p_s = 1.07 \quad \Rightarrow \quad p_s = 141.93 \text{ mm}$$

31. Vapour pressure of pure liquid A (p_A°) = 450 mm

Vapour pressure of pure liquid B (p_B°) = 700 mm

Total vapour pressure of the solution (p) = 600 mm

According to Raoult'a law,

$$p = p_A^\circ \chi_A + p_A^\circ \chi_B = p_A^\circ \chi_A + p_B^\circ (1 - \chi_A)$$

$$(600 \text{ mm}) = 450 \text{ mm} \times \chi_A + 700 \text{ mm } (1 - \chi_A)$$

$$= 700 \text{ mm} + \chi_A (450 - 700) \text{ mm}$$

$$= 700 - \chi_A (250 \text{ mm})$$

$$\chi_A = \frac{(600 - 700)}{-(250 \text{ mm})} = 0.40$$

Mole fraction of A (χ_A) = 0.40

Mole fraction of B (χ_B) = 1 − 0.40 = 0.60

$$p_A = p_A^\circ \chi_A = (450 \text{ mm}) \times 0.40 = 180 \text{ mm}$$

$$p_B = p_B^\circ \chi_B = (700 \text{ mm}) \times 0.60 = 420 \text{ mm}$$

Mole fraction of A in vapour phase

$$= \frac{p_A}{p_A + p_B} = \frac{(180) \text{ mm}}{(180 + 420) \text{ mm}} = 0.30$$

Mole fraction of B in vapour phase

$$= \frac{p_B}{p_A + p_B} = \frac{(420) \text{ mm}}{(180 + 420) \text{ mm}} = 0.70$$

32. ***Step* I Calculation of vapour pressure of pure liquid A (p_A°)**

Number of moles of liquid A

$$(n_A) = \frac{W_A}{M_A} = \frac{(100 \text{ g})}{(140 \text{ g mol}^{-1})} = 0.7143 \text{ mol}$$

Number of moles of liquid B

$$(n_B) = \frac{W_B}{M_B} = \frac{(1000 \text{ g})}{(180 \text{ g mol}^{-1})} = 5.5556 \text{ mol}$$

Mole fraction of A

$$(\chi_A) = \frac{n_A}{n_A + n_B} = \frac{(0.7143 \text{ mol})}{(0.7143 + 5.5556) \text{ mol}}$$

$$= \frac{0.7143}{6.2699} = 0.1139$$

Mole fraction of B (χ_B) = 1 − 0.1139 = 0.8861

Vapour pressure of pure liquid B (p_B°) = 500 torr

Total vapour pressure of solution (p) = 475 torr

According to the Raoult's law

$$p = p_A^\circ \chi_A + p_B^\circ \chi_B$$

$$475 \text{ torr} = p_A^\circ \times (0.1139) + 500 \text{ torr} \times (0.8861)$$

$$475 \text{ torr} = p_A^\circ \times (0.1139) + 443.05 \text{ torr}$$

$$p_A^\circ = \frac{(475 - 443.05) \text{ torr}}{(0.1139)} = \frac{31.95}{0.1139} \text{ torr} = 280.5 \text{ torr}$$

***Step* II Calculation of vapour pressure of A in the solution (p_A)**

According to Raoult's law,

$$p_A = p_A^\circ \chi_A = (280.5 \text{ torr}) \times (0.1139) = 32.0 \text{ torr}$$

33. For ideal solution,

$$p = \chi'_A \, p^\circ_A + \chi'_B \, p^\circ_B$$

$$\because \quad \chi'_A = 0.4, \; \chi'_B = 0.6$$

$$p^\circ_A = 7 \times 10^3 \text{ Pa}, \; p^\circ_B = 12 \times 10^3 \text{ Pa}$$

On substituting the given values in Eq. (i), we get

$$p = 0.4 \times 7 \times 10^3 + 0.6 \times 12 \times 10^3$$

$$= 10 \times 10^3 \text{ Pa} = 1 \times 10^4 \text{ Pa}$$

In vapour phase,

$$\chi_A = \frac{p_A}{p} = \frac{\chi'_A \, p^\circ_A}{p} = \frac{0.4 \times 7 \times 10^3}{1 \times 10^4} = 0.28$$

$$\therefore \quad \chi_B = 1 - 0.28 = 0.72 \qquad [\because \; \chi_A + \chi_B = 1]$$

34. For a solution of volatile liquids the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. This is known as Raoult's law. Liquid M and N form an ideal solution. Vapour pressures of pure liquids M and N are 450 and 700 mm Hg respectively.

$$\therefore \quad p^\circ_N > p^\circ_M$$

So, by using Raoult's law

$$y_N > x_N \qquad \ldots(\text{i})$$

and

$$x_M > y_M \qquad \ldots(\text{ii})$$

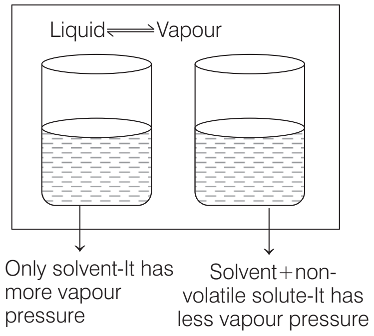
Multiplying (i) and (ii) we get

$$y_N \, x_M > y_M \, x_N$$

$$\therefore \quad \frac{x_M}{x_N} > \frac{y_M}{y_N}$$

Thus, correct relation is (a).

35.



If a non-volatile solute is added to a solvent to form a solution, the vapour pressure gets decreased.

$\therefore$ According to Raoult's law, if vapour pressure of pure solvent is p°, vapour pressure of solvent in solution (p) is $= p^\circ \cdot x_A$.

$$\therefore \qquad p < p^\circ$$

Since, vapour pressure of solution is less, there will be net backward reaction [i.e. vapour $\longrightarrow$ liquid] in that beaker. Thus, its volume increases.

In another beaker containing only net reaction is forward,

Thus, volume decreases.

36. The incorrect statement among the given statements is (c) and the explanation of all the statements is as follows

According to Raoult's law, vapour pressure of the solution p_{ideal} (ideal vapour pressure)

$$= p_A^\circ + (p_B^\circ - p_A^\circ)\chi_B$$

(A = solvent : acetone, B = solute : CS_2)

Given; $p_A^\circ = 344$ mmHg, $p_B^\circ = 512$ mmHg.

$\therefore \qquad p_{\text{ideal}} = 3.44 + (512 - 344)\chi_B$

or $\qquad p_{\text{ideal}} = 344 + 168\,\chi_B$ and so, $0 < \chi_B < 1$.

Also, total vapour pressure (p) = 600 mmHg

$\therefore$ For any value of χ_B, $p > p_{\text{ideal}}$.

Since $p \neq p_{\text{ideal}}$, so, option (a) is correct.

Option (b) is also correct. Since $p > p_{\text{ideal}}$, (i.e. positive deviation) therefore attractive force between CS_2 and acetone is weaker than CS_2—CS_2 or acetone-acetone attraction.

Option (c) is incorrect as for positive deviation, $\Delta V > 0$ because final volume of solution must be greater than the sum of volumes of components taken.

Option (d) is correct. Since, in such solution, $\Delta_{\text{mix}}H$ is positive because energy is required to break A—A and B—B bonds.

37. Mole fraction of P, $(\chi_P) = \dfrac{3}{3+2} = \dfrac{3}{5}$

Mole fraction of Q. $(\chi_Q) = \dfrac{2}{3+2} = \dfrac{2}{5}$

$$P_{\text{total}} = \chi_P \; 5 \; \chi_P^0 + \chi_Q \times \chi_Q^0$$
$$= \frac{3}{5} \times 80 + \frac{2}{5} \times 60 = 48 + 24 = 72 \text{ torr}$$

38. When $X_B = 0$, we have pure A

$\therefore \qquad p_A^\circ = 120 - 80 \times 0 = 120$ mm

The given expression can be rewritten as

$$p = 120 - 80(1 - X_A)$$

When $X_A = 0$, we have pure B

$\therefore \qquad p_B^\circ = 120 - 80(1 - 0) = 120 - 80 = 40$ mm

39. $(\chi_A)_{\text{vapour}} = \dfrac{p_A}{p_{\text{total}}} = \dfrac{(\chi_A)_{\text{liquid}}\, p_A^\circ}{p_{\text{total}}}$ or $\dfrac{(\chi_A)_{\text{vapour}}}{(\chi_A)_{\text{liquid}}} = \dfrac{p_A^\circ}{p_{\text{total}}}$

As B is less volatile, $p_{\text{total}} < p_A^\circ$

$\therefore \quad \dfrac{(\chi_A)_{\text{vapour}}}{(\chi_A)_{\text{liquid}}}$ or $(\chi_A)_{\text{vapour}} > (\chi_A)_{\text{liquid}}$

40. p_{total} (expected from Raoult's law) $= \chi_A p_A^\circ + \chi_B\, p_B^\circ$

$= \dfrac{1}{3} \times 150 + \dfrac{2}{3} \times 240 = 50 + 160 = 210$ torr which is greater than the experimental value of 200 torr. As observed vapour pressure is less that expected from Raoult's law, it shows – ve deviation from Raoult's law.

41. There is H-bonding in ethyl alcohol which is cut off on adding *n*-heptane. Hence, it shows positive deviations.

42. On mixing acetone and chloroform, dipole-dipole interactions take place. Hence, negative deviation from Raoult's law is observed.

43. Ethanol + water form a non-ideal solution showing + ve deviation from Raoult's law. Hence, ΔH = + ve, i.e. there is absorption of heat and ΔV = + ve, i.e. there is increase in volume.

44. In CS_2-acetone, A—B interactions are weaker than A—A, B—B interactions.

45. HNO_3 + H_2O solution shows negative deviation from ideal behaviour and hence it forms azeotropic with maximum boiling point.

46. $\dfrac{p^\circ - p_s}{p^\circ}$ = molality $\times (1 - \alpha + x\alpha + y\alpha)$

The value of $p^\circ - p_s$ is maximum for $BaCl_2$.

47. Due to addition of nitric acid in water, the vapour pressure of pure water decreases.

48. Relative lowering in vapour pressure,

$$\frac{p^\circ - p_s}{p^\circ} = \frac{w}{m} \times \frac{M}{W}$$
$$\frac{0.30 \text{ mm}}{17.54 \text{ mm}} = \frac{20}{m} \times \frac{18}{100}$$
$$\Rightarrow \qquad m = \frac{20 \times 18 \times 17.54}{0.30 \times 100} = 210.48$$

49. w_B (solute) = 25 g ; $M_B = 180$ g mol^{-1}; $p_A^\circ = 17.535$ mm

w_A (water) = 450 g; $M_A = 18$ g mol ; p_s = ?

$$\frac{p_A^\circ - p_s}{p_A^\circ} = \chi_B = \frac{n_B}{n_B + n_A}$$
$$n_B = \frac{w_B}{M_B} = \frac{25}{180} = 0.1389$$
$$n_A = \frac{w_A}{M_A} = \frac{450}{18} = 25$$
$$\frac{17.535 - p_s}{17.535} = \frac{0.1389}{0.1389 + 25}$$
$$\frac{17.535 - p_s}{17.535} = 0.00552$$
$$p_s = 17.535 - 0.097$$
$$p_s = 17.438 \text{ mmHg}$$

50. The unit of ebullioscopic constant is K kg mol^{-1} or K (molality)$^{-1}$.

51. $\Delta T_f = 1.86 \times \frac{342}{342} = 1.86° \text{ C}$

$\therefore T_f = T - \Delta T_f = 0 - 1.86 = -1.86° \text{ C}$

52. From depression in freezing point expression,

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

$$62 = \frac{1000 \times 1.86 \times 50}{9.3 \times W}$$

$$W = 161.3 \text{ g}$$

Total water = 200 g

Hence, ice separated = (200 – 161.3) g = 38.7 g

53. $i = 1 + \alpha$

$$= \frac{\text{cal. mol. weight}}{\text{exp. mol. wt}} = \frac{58.5}{30} = 1.95$$

$\therefore 1 + \alpha = 1.95$

$\alpha = 0.95$

55. In the figure water will move from side (*B*) to side (*A*) if a pressure greater than osmotic pressure is applied on piston (*B*). Thus, (b) is the correct option.

56. An unripe mango placed in a concentrated salt solution to prepare pickle, shivels because it loses water due to osmosis.

58. $p = \frac{w}{mV} RT$, since, wRT/V are constant thus, $p \propto \frac{1}{m}$

$\therefore \qquad p_2 > p_1 > p_3$

59. Molarity of urea $= \dfrac{\frac{6}{60}}{\frac{100}{1000}} = 1$ M

Hence, 1 M solution of glucose is isotonic with 6% urea solution.

60. $C = \frac{5}{342} \times \frac{1}{100} \times 1000 = \frac{50}{342}$ mol/L

$$\pi = \frac{50}{342} \times 0.082 \times 423 = 5.07 \text{ atm}$$

61. For isotonic solution

$$\frac{w_1}{m_1} = \frac{w_2}{m_2} \Rightarrow \frac{5}{342} = \frac{1}{m_2} \Rightarrow m_2 = \frac{342}{5} = 68.4$$

62. $\pi = CRT = \frac{W_B \times R \times T}{M_B \times V}$

For both the solutions, *R*, *T* and *V* are constants.

For I solution

$$(4.98 \text{ bar}) = \frac{(36 \text{ g}) \times R \times T}{(180 \text{ g mol}^{-1}) \times V} \qquad \ldots\text{(i)}$$

For II solution

$$(1.52 \text{ bar}) = \frac{W_B \times R \times T}{M_B \times V} \qquad \ldots\text{(ii)}$$

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

$$\frac{(1.52 \text{ bar})}{(4.98 \text{ bar})} = \frac{W_B \times R \times T}{M_B \times V} \times \frac{180 \times V}{36 \times R \times T}$$

$$\frac{W_B}{M_B} = \frac{1.52}{4.98 \times 5} = 0.0610 \text{ mol L}^{-1}$$

64. ΔT_f = Freezing point of H_2O – Freezing point of ethylene glycol solution

$= 0 - (-6°) = 6°$

$K_f = 1.66°$ K kg mol^{-1}

w_1 = mass of ethylene glycol in grams

w_2 = mass of sovent (H_2O) in grams = 4000 g

m_1 = molar mass of ethylene glycol = 62 g mol^{-1}

$$\Delta T_f = \frac{1000\, K_f w_1}{m_1 w_2} \Rightarrow 6 = \frac{1000 \times 1.86 \times w_1}{62 \times 4000}$$

$w_1 = 800$ g

65. $\because \quad \Delta T_b = K_b \times m$

$$m = \frac{\Delta T_b}{K_b} = \frac{0.128}{0.512} = 0.25$$

Now, $\qquad K_f = 1.86°\text{ C}, m = 0.25$

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

$\therefore \qquad \Delta T_f = 1.86 \times 0.25 = 0.465° \text{ C}$

$\therefore$ Freezing point of the solution $(T_b) = T° - \Delta T_f$

$= 0 - 0.465 = -0.465°$ C

66. 1.00 kg contains 0.100 kg CH_3OH (and 0.900 kg H_2O)

$$(100 \text{ g } CH_3OH)\left(\frac{1 \text{ mol}}{32.0 \text{ g}}\right) = 3.12 \text{ mol} = \frac{3.12 \text{ mol}}{0.900 \text{ kg}} = 3.47 \text{ m}$$

$$\Delta T_f = K_f \times m = (1.86° \text{ C/m})(3.47 \text{ m}) = 6.45° \text{ C}$$

Freezing point of the solution $(T_b) = T° - \Delta T_f = 0 - 6.45$

$= -6.45°$ C

67. $\Delta_f = \frac{100\, K_f\, w_2}{w_1\, M_2}$

For AB_2, $2.3 = \frac{1000 \times 5.1 \times 1}{20 \times M_{AB_2}}$ or $M_{AB_2} = 110.87$

For AB_4, $1.3 = \frac{1000 \times 5.1 \times 1}{20 \times M_{AB_2}}$ or $M_{AB_4} = 196.15$

Suppose atomic mass of $A = a$ and that of $B = b$. Then

$$a + 2b = 110.87 \text{ and } a + 42.64 \simeq 42{,}6$$

On solving, we get

$$a = 25.59 \simeq 25.6 \text{ and } b = 42.64 = 196.15$$

68. All other factors remaining the same, $\Delta T_f \propto$ molar concentration

$$\frac{(\Delta T_f)_1}{(\Delta T_f)_2} = \frac{C_1}{C_2}$$

Molar concentration after mixing can be calculated as

$$M_1V_1 + M_2V_2 = M_3(V_1 + V_2)$$

$$0.01 \times V + 0.002\, V = M_3(2V) \text{ or } M_3 = \frac{0.012}{2} = 0.006$$

$$\frac{0.18}{(\Delta T_f)_2} = \frac{0.01}{0.006} \text{ or } (\Delta T_f)_2 = 0.108$$

$\therefore$ T_f of solution after mixting $= 0 - 0.108 = -0.108$°C

69. $$M_2 = \frac{1000\,K_f\,w_2}{w_1\,\Delta T_f} = \frac{1000\,w_2}{w_1\,\Delta T_f} \times \frac{RT_0^2}{1000\,L_f}$$

$$= \frac{1000\times 2.423}{100\times 0.661} \times \frac{2(353.1)^2}{1000\times 35.7} = 256 \text{ g mol}^{-1}$$

If S_x is the formula, then molecular mass

$$= x \times 23 = 256 \text{ or } x = 8$$

70. $BaCl_2$ gives maximum ion hence, it shows lowest vapour pressure.

71. Elevation in bp $= iK_b \cdot m$

If k_b and m are same,

Elevation in boiling point $\propto i$

$$NaOH \longrightarrow \underbrace{Na^+ + OH^-}_{2 \text{ ions}}$$

$$Na_2SO_4 \longrightarrow \underbrace{2Na^+ + SO_4^{2-}}_{3 \text{ ions}}$$

$$NH_4NO_3 \longrightarrow \underbrace{NH_4^+ + NO_3^-}_{2 \text{ ions}}$$

$$KNO_3 \longrightarrow \underbrace{K^+ + NO_3^-}_{2 \text{ ions}}$$

72. Osmotic pressure is a colligative property.

Osmotic pressure $\propto$ no. of particles

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

Concentration of particles $= 2 \times 2M = 4M$

Glucose does not dissociate

$\therefore$ Concentration of particles $= 1 \times 1\text{ M} = 1\text{ M}$

Urea does not dissociate,

$\therefore$ Concentration of urea $= 1 \times 2\text{ M} = 2\text{ M}$

$\therefore$ Glucose solution will have minimum osmotic pressure.

73. Actual molecular weight of naphthoic acid ($C_{11}H_8O_2$) $= 172$

$$\text{Molecular mass (calculated)} = \frac{1000 \times K_f \times w}{W \times \Delta T_f}$$

$$= \frac{1000 \times 1.72 \times 20}{50 \times 2} = 344$$

$$\text{van't Hoff factor } (i) = \frac{\text{actual mol. wt.}}{\text{calculated mol. wt.}} = \frac{172}{344} = 0.5$$

74. $$\Delta T_f = i \times K_f \times m$$

$$7.10 \times 10^{-3} = i \times 1.86 \times 0.001$$

$$i = 3.817$$

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

$$1 = \frac{3.817 - 1}{(x+1) - 1} \Rightarrow x = 2.817 \approx 3$$

$\therefore$ Molecular formula of the compound is $K_3[Fe(CN)_6]$.

75.
$$\begin{array}{lccc} & CuCl_2 & \rightleftharpoons Cu^{2+} & +2Cl^- \\ \text{Before ionisation} & 1 \text{ mol} & 0 & 0 \\ \text{After ionisation} & (1-\alpha) & \alpha & 2\alpha \end{array}$$

Thus, number of particles after ionisation

$$= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$

$$\therefore \text{vant' Hoff factor } (i) = \frac{1+2\alpha}{1} \text{ (On 100\% ionisation, } \alpha = 1)$$

$$i = \frac{1 + 2 \times 1}{1} = 3$$

The elevation of boiling point, $\Delta T_b = 3 \times K_b \times m$

Molality of $CuCl_2$ solution

$$(m) = \frac{\text{wt. of } CuCl_2 \text{ in g / mol wt. of } CuCl_2}{\text{wt. of water in kg}}$$

$$= \frac{\frac{13.44}{134.4}}{1} = 0.1 \text{ m}$$

Thus, $\Delta T_b = 3 \times 0.52 \times 0.1 = 0.156°\text{ C} \approx 0.16°\text{ C}$

76. $$\underset{(1-\alpha)}{HBr} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{Br^-}$$

$$i_{\text{total}} = (1-\alpha) + \alpha + \alpha = (1 + \alpha)$$

$$i = 1 + 0.9 = 1.9$$

$$\Delta T_f = iK_f m = 1.9 \times 1.86 \times \frac{8.1}{81} \times \frac{1000}{100}$$

$$= 3.53°\text{ C}$$

$$T_f = T - \Delta T_f = 0 - 3.53°\text{ C} = -3.53°\text{ C}$$

77. According to van't Hoff equation,

$$\text{Osmotic pressure } (\pi) = i\,CRT = \frac{in_B RT}{V}$$

$i = 2.47$; $V = 2.5$ L; $R = 0.0821 \text{ L atm K}^{-1}\text{mol}^{-1}$

$T = 27 + 273 = 300$ K; $\pi = 0.75$ atm

$$n_B = \frac{\pi V}{iRT} = \frac{(0.75 \text{ atm}) \times (2.5 \text{ L})}{(2.47) \times (0.0821 \text{ L atm K}^{-1}\text{mol}^{-1}) \times (300 \text{ K})}$$

$$= 0.0308 \text{ mol}$$

Amount of $CaCl_2$ dissolved $= n_B \times M_B$

$$= (0.0308 \text{ mol}) \times (111 \text{ g mol}^{-1})$$

$$= 3.42 \text{ g}$$

78. Amount of K_2SO_4 dissolved $= 25 \text{ mg} = 0.025$ g

Volume of solution $= 2$ L

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

Molar mass of

$K_2SO_4 = (2 \times 39) + (32) + (4 \times 16) = 174 \text{ g mol}^{-1}$

Since, K_2SO_4 dissociates completely as,

$$K_2SO_4 \xrightarrow{Aq} 2K^+ + SO_4^{2-}$$

Total ions produced after dissociation (per mol) = 3

$$\text{So, } i = 3,\quad \pi = iCRT = i \times \frac{n}{V} RT = \frac{i \times W \times R \times T}{M \times V}$$

$$= \frac{3 \times (0.025 \text{ g}) \times (0.0821 \text{ L atm K}^{-1}\text{mol}^{-1}) \times (298 \text{ K})}{(174 \text{ g mol}^{-1}) \times (2 \text{ L})}$$

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

79. ***Step*** **I Calculation of van't Hoff factor of acid**

$\Delta T_f = 1^\circ\text{C} = 1\ \text{K};\ K_f = 1.86\ \text{K kg mol}^{-1}$

$\Delta T_f = i\, K_f\, m$

or $$i = \frac{\Delta T_f}{K_f m} \qquad \ldots\text{(i)}$$

$$m = \frac{W_B}{M_B \times W_A} = \frac{(19.5\ \text{g})}{(78\ \text{g mol}^{-1}) \times (0.5\ \text{kg})}$$

$$= 0.5\ \text{mol kg}^{-1} \qquad \ldots\text{(ii)}$$

Placing the values in Eq. (i), we find the value of van't Hoff factor (i)

$$i = \frac{1}{(1.86\ \text{K kg mol}^{-1}) \times (0.5\ \text{mol kg}^{-1})} = 1.0753$$

Step **II Calculation of degree of dissociation of the acid**

Suppose degree of dissociation at the given concentration is α.

$$\begin{array}{llll} & \text{CH}_2\text{FCOOH} & \underset{}{\overset{aq}{\rightleftharpoons}}\ \text{CH}_2\text{FCOO}^- & +\ \text{H}^+ \\ \text{Initial conc. } C \text{ mol kg}^{-1} & & 0 & 0 \\ \text{At equilibrium} & C\,(1-\alpha) & C\alpha & C\alpha \end{array}$$

$$\text{Total} = C(1+\alpha)$$

$$\therefore \qquad i = \frac{C\,(1+\alpha)}{C} = 1 + \alpha$$

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

Step **III Calculation of dissociation constant for the acid**

$$\text{(Molal) } C = 0.5\ \text{m} \qquad \text{(From Eq. (ii))}$$

$$K_a = \frac{[\text{CH}_2\ \text{FCOO}^-]\ [\text{H}^+]}{[\text{CH}_2\ \text{FCOOH}]} = \frac{C\alpha \cdot C\alpha}{C\,(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$K_a = \frac{(0.5)\ (0.0753)^2}{(1-0.0753)} = \frac{(0.5) \times (0.0753)^2}{(0.9247)} = 3.07 \times 10^{-3}$$

80. $\text{KCl} \longrightarrow \text{K}^+ + \text{Cl}^-$

$$\alpha = \frac{i-1}{n-1} \quad \text{or} \quad 0.82 = \frac{i-1}{2-1} \quad \text{or} \quad i = 1.82$$

$$\pi V = i\,\frac{W_B}{M_B} \times RT$$

Volume of solution $= 100\ \text{mL} = \dfrac{100}{1000}\ \text{L}$

$$\pi \times \frac{100}{1000} = 1.82 \times \frac{1}{74.5} \times 0.083 \times 291$$

$$\pi = \frac{439.58}{74.5} = 5.9\ \text{bar}$$

81. Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature, $\pi = CRT$

Concentration of $\text{BaCl}_2 = 0.01\ \text{M}$ (Given)

$$\pi_{XY} = 4\pi_{\text{BaCl}_2} \qquad \text{(Given)}$$

$$i \times CRT = 4 \times i \times CRT \qquad \ldots\text{(i)}$$

For the calculation of i,

$$XY \longrightarrow X^+ + Y^- \qquad \text{(Here, } i = 2\text{)}$$

$$\text{BaCl}_2 \longrightarrow \text{Ba}^{2+} + 2\text{Cl}^- \qquad \text{(Here, } i = 3\text{)}$$

Putting the values of i in (i)

$$2 \times [XY] = 4 \times 3 \times [\text{BaCl}_2]$$

$$2 \times [XY] = 12 \times 0.01$$

$$[XY] = \frac{12 \times 0.01}{2}$$

So, the concentration of $XY = 0.06\ \text{mol L}^{-1}$

$$= 6 \times 10^{-2}\ \text{mol L}^{-1}$$

82. Given 100 mL of urea solution is mixed with 100 mL of cane-sugar and therefore, total volume of solution becomes 200 mL in which 3.4 urea and 1.6 g sugar is present

$\therefore \pi_{\text{sugar}} \times (200/1000) = (1.6/342) \times 0.821 \times 293$

$\therefore\ \pi_{\text{sugar}} = 0.56\ \text{atm}$

$\therefore \pi_{\text{urea}} \times (200/1000) = (3.4/60) \times 0.0821 \times 293$

$\therefore \pi_{\text{urea}} = 6.82\ \text{atm}$

Total $\pi = \pi_{\text{sugar}} + \pi_{\text{urea}}$

$$= 0.56 + 6.82 = 7.38\ \text{atm}$$

83. Elevation in boiling point $(\Delta T_b) = K_b \times m \times i$

Depression is freezing point $(\Delta T_f) = K_f \times m \times i$

where, m = molality

For the glucose solution (van't Hoff factor, $i = 1$),

$$\Delta T_b^{1m} = \Delta T_f^{2m} = 2K$$

So, $$K_b \times 1 \times 1 = K_f \times 2 \times 1$$

$\Rightarrow$ $$K_b = 2K_f$$

84. Let the degree of association of acetic acid (CH_3COOH) in benzene is α, then

$$\begin{array}{lll} & 2\text{CH}_3\text{COOH} \rightleftharpoons & (\text{CH}_3\text{COOH})_2 \\ \text{Initial moles} & 1 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & \dfrac{\alpha}{2} \end{array}$$

$$\therefore \text{Total moles} = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} \quad \text{or} \quad i = 1 - \frac{\alpha}{2}$$

Now, depression in freezing point (ΔT_f) is given as

$$\Delta T_f = i\,K_f m \qquad \ldots\text{(i)}$$

where, K_f = molal depression constant or cryoscopic constant.

m = molality

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{weight of solvent (in kg)}} = \frac{0.2}{60} \times \frac{1000}{20}$$

Putting the values in Eq. (i)

$$\therefore \qquad 0.45 = \left[1 - \frac{\alpha}{2}\right](5.12)\left[\frac{0.2}{60} \times \frac{1000}{20}\right]$$

$$1 - \frac{\alpha}{2} = \frac{0.45 \times 60 \times 20}{5.12 \times 0.2 \times 1000}$$

$$\Rightarrow \qquad 1 - \frac{\alpha}{2} = 0.527$$

$$\Rightarrow \qquad \frac{\alpha}{2} = 1 - 0.527$$

$$\therefore \qquad \alpha = 0.946$$

Thus, percentage of association = 94.6%

85. Considering the expression of the depression in freezing point of a solution,

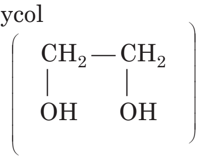
$$\Delta T_f = K_f \times m \times i$$

$$T_f^\circ - T_f = K_f \times \frac{w_B \times 1000}{M_B \times w_A (\text{in g})} \times i \qquad \ldots(\text{i})$$

Here, $T_f^\circ = 0^\circ \text{C}$, $T_f = -10^\circ\text{C}$

w_B = mass of ethylene glycol = 62 g

M_B = molar mass of ethylene glycol



$$\left(\begin{array}{cc} CH_2 — CH_2 \\ | \quad\quad | \\ OH \quad\; OH \end{array}\right)$$

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

w_A = mass of water in g as liquid solvent,

i = van't-Hoff factor = 1

(for ethylene glycol in water)

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

On substituting in Eq. (i), we get

$$0 - (-10) = 1.86 \times \frac{62 \times 1000}{62 \times w_A} \times 1$$

$$\Rightarrow \qquad w_A = \frac{1.86 \times 62 \times 1000}{10 \times 62} = 186 \text{ g}$$

So, amount of water separated as ice (solid solvent)

$$= 250 - w_A = (250 - 186) \text{ g} = 64 \text{ g}$$

86. Depression in freezing point (ΔT_f) is given by

$\Delta T_f = iK_f m$

i = vant Hoff factor

K_f = molal depression constant

m = molality

For K_2SO_4, $i = 3$

It can be verified by the following equation :

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$$

Using formula

$$\Delta T_f = iK_f \times m = 3 \times 4 \times 0.03 = 0.36 \text{ K}$$

87. For dilute solution, lowering of vapour pressure $(\Delta p) = p^0 - p$ and relative lowering of vapour pressure $= \frac{\Delta p}{p^0}$ which is a colligative property of solutions.

$$\frac{\Delta p}{p^0} = \chi_B \times i$$

$$\Rightarrow \qquad \Delta p = \chi_B \times i \times p^0$$

where, p^0 = vapour pressure of pure solvent

i = van't Hoff factor

χ_B = mole fraction of solute

Given,

p° = vapour pressure of pure water of 25° C

= 35 mmHg

χ_B = mole fraction of solute (urea)

$$= \frac{n_B}{n_A + n_B} = \frac{\frac{0.60}{60}}{\frac{360}{18} + \frac{0.60}{60}} = \frac{0.01}{20 + 0.01} = \frac{0.01}{20.01} = 0.0005$$

i = van't Hoff factor = 1 (for urea)

Now, according to Raoult's law, $\Delta p = \chi_B \times i \times p^\circ$

On substituting the above given values, we get

$$\Delta p = 0.0005 \times 1 \times 35 = 0.0175 \text{ mmHg}$$

88. The expression of elevation of boiling point,

$$\Delta T_b = K_b \times m \times i = k_b \times \frac{w_2 \times 1000}{M_2 \times w_1} \times i$$

where, m = molality

i = van't Hoff factor = 1 (for non-electrolyte/non-associable)

w_2 = mass of solute in g = 1 g (present in both of the solutions)

M_2 = molar mass of solute in g mol^{-1} (same solute in both of the solutions)

w_1 = mass of solvent in g = 100 g (for both of the solvents A and B)

K_b = ebullioscopic constant

So, the expression becomes,

$$\Delta T_b \propto K_b$$

$$\Rightarrow \quad \frac{\Delta T_b(A)}{\Delta T_b(B)} = \frac{K_b(A)}{K_b(B)} = \frac{1}{5} \qquad \left[\text{Given, } \frac{K_b(A)}{K_b(B)} = \frac{1}{5}\right]$$

89. We know that,

Depression in freezing points (ΔT_f)

$$T^\circ{}_f - T_f = K_f \times m \times i$$

where, K_f = molal depression constant

$$m = \text{molality} = \frac{w_{\text{solute}} \times 1000}{M_{\text{solute}} \times w_{\text{solvent (in g)}}}$$

i = van't Hoff factor

For diluted milk

$$\Delta T_{f_1} = K_f \times m_1 \times i$$

$$\Rightarrow 0 - (0.2) \Rightarrow 0.2 = K_f \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_1(H_2O)} \times 1$$

For pure milk $\Delta T_{f_2} = K_f \times m_2 \times i$

$$\Rightarrow 0 - (-0.5) = 0.5 = K_f \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_2(H_2O)} \times 1$$

$$\text{So,} \frac{0.2}{0.5} = \frac{K_f}{K_f} \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_1(H_2O)} \times \frac{M_{\text{milk}} \times w_2(H_2O)}{w_{\text{milk}} \times 1000}$$

$$= \frac{w_2(H_2O)}{w_1(H_2O)}$$

$$\Rightarrow \quad \frac{w_2(H_2O) \text{ (in pure milk)}}{w_1(H_2O) \text{ (in diluted milk)}} = \frac{2}{5}$$

i.e. 3 cups of water has to be added to 2 cups of pure milk.

90. The ionisation of K_2HgI_4 in aqueous solution is as follows

$$K_2[HgI_4] \rightleftharpoons 2K^+ + [HgI_4]^{2-}$$

van't Hoff factor (i) for ionisation reaction is given as,

$$i = 1 + \alpha(n-1)$$

where, n = number of ions,

α = degree of ionisation or dissociation

From above equation, it is clear that $n = 3$

$$i = 1 + 0.4\,(3-1)$$

[Given, % $\alpha = 40\%$ or $\alpha = 0.4$]

$$= 1.8$$

91. Molecules of benzoic acid dimerise in benzene as:

$$2(C_6H_5COOH) \rightleftharpoons (C_6H_5COOH)_2$$

Now, we know that depression in freezing point (ΔT_f) is given by following equation:

$$\Delta T_f = i \times K_f \times m = \frac{i \times K_f \times w_{\text{solute}} \times 1000}{Mw_{\text{solute}} \times w_{\text{solvent}}} \quad \text{...(i)}$$

Given, w_{solute} (benzoic acid) = w g

w_{solvent} (benzene) = 30 g

Mw_{solute} (benzoic acid) = 122 g mol^{-1}, $\Delta T_f = 2$ K

$K_f = 5$ Kkg mol^{-1}, % $\alpha = 80$ or $\alpha = 0.8$

$$\begin{array}{lcc} & 2(C_6H_5COOH) \rightleftharpoons & (C_6H_5COOH)_2 \\ \text{Initial} & 1 & 0 \\ \text{Final} & 1-\alpha & \alpha/2 \\ & = 1-0.8 = 0.2 & 0.8/2 = 0.4 \end{array}$$

Total number of moles at equilibrium

$$= 0.2 + 0.4 = 0.6$$

$$i = \frac{\text{Number of moles at equilibrium}}{\text{Number of moles present initially}}$$

$$i = \frac{0.6}{1} = 0.6$$

On substituting all the given values in Eq. (i), we get

$$2 = \frac{0.6 \times 5 \times w \times 1000}{122 \times 30},\ w = 2.44 \text{ g}$$

Thus, weight of acid (w) is 2.4 g.

Round II

1. ***Step* I Calculation of partial pressure of oxygen and nitrogen**

Partial pressure of O_2

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

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

$$= 7.9 \times 760 \text{ mm}$$

***Step* II Composition of O_2 and N_2 dissolved in water**

The amount of gases dissolved in water is calculated in terms of their mole fractions.

$$\chi_{O_2} = \frac{p_{O_2}}{K_H} = \frac{(2 \times 760 \text{ mm})}{(3.30 \times 10^7 \text{ mm})} = 4.6 \times 10^{-5}$$

$$\chi_{N_2} = \frac{p_{N_2}}{K_H} = \frac{(7.9 \times 760 \text{ mm})}{(6.51 \times 10^7 \text{ mm})} = 9.22 \times 10^{-5}$$

2. ***Step* I Calculation of number of moles of CO_2**

According to Henry's law,

$$\text{Mole fraction of } CO_2\ (\chi_{CO_2}) = \frac{\text{partial pressure of } CO_2}{K_H \text{ for } CO_2}$$

$$K_H = 1.67 \times 10^8 \text{ Pa} = \frac{(1 \text{ atm})}{(101325 \text{ Pa})} \times (1.67 \times 10^8 \text{ Pa})$$

$$= 1.648 \times 10^3 \text{ atm}$$

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

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

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

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

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

$$= 0.0422 \text{ mol}$$

Note n_{CO_2} is considered negligible due to its little solubility in water.

***Step* II Calculation of mass of dissolved CO_2 in water**

Mass of CO_2 = no· of moles of CO_2 × molar mass of CO_2

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

$$= 1.857 \text{ g}$$

3. $m = 1.5 \times 10^{-3}$ m or 1.5×10^{-3} mol kg^{-1}

Mass of solute = 1.5×10^{-3} g or 1.5 mg

Mass of solvent = ?

Molar mass of solute

$$(C_{19}H_{21}NO_3) = (12 \times 19) + (1 \times 21) + (14) + (16 \times 3)$$

$$= 311 \text{ g mol}^{-1}$$

$$\text{Number of moles of solute} = \frac{\text{mass}}{\text{molar mass}}$$

$$= \frac{(1.5 \times 10^{-3} \text{ g})}{(311 \text{ g mol}^{-1})}$$

$$\text{Molality } (m) = \frac{\text{number of moles}}{\text{mass of solvent in kg}}$$

$$\text{Mass of solvent} = \frac{\text{number of moles}}{\text{molality}}$$

$$= \frac{(1.5 \times 10^{-3} \text{ g})}{(311 \text{ g mol}^{-1})} \times \frac{1}{(1.5 \times 10^{-3} \text{ mol kg})}$$

$$= \frac{1}{311} = 0.0032 \text{ kg or } 3.2 \text{ g}$$

5. HgI_2 although insoluble in water but shows complex formation with KI and therefore, freezing point decreases.

6. (ii) 0.1 M glucose, $\pi = CRT = 0.1RT$

(iii) 0.6 g urea in 100 mL solution

$$\pi = \frac{n}{V}RT = \frac{w/m}{V}RT = \frac{0.6/60 \times 1000}{100} \times RT = 0.1\,RT$$

(iv) 1.0 g of non electrolyte solute (*X*) is 50 mL solution

$$\pi = \frac{1.0/200}{50} \times 1000RT = 0.1\ RT$$

Hence, option (ii), (iii), (iv) have same osmotic pressure, osmotic pressure of 0.1 M NaCl is higher than (ii), (iii), (iv) because it dissociates to give maximum number or particles.

7. $m = \frac{\Delta T_b}{K_b} = \frac{-0.060}{-1.86} = 3.2 \times 10^{-2} = 0.032$

i.e. 0.032 = total particles

$\therefore$ The number of $H^+ = (0.032 - 0.025)$ m $= 0.007$ M H^+

$$HA \rightleftharpoons H^+ + A^-$$

$$[H^+] = [A^-] = 0.007 \text{ M}$$

$$\therefore \qquad HA = 0.018$$

$$K_a = \frac{(0.007)^2}{0.018} = 3 \times 10^{-3}$$

$$\text{p}K_a = -\log K_a = -\log(3 \times 10^{-3}) = 2.5$$

8. Boiling point $(T_b) = 100 + \Delta T_b = 100 + K_b m$

Freezing point $(T_f) = 0 - \Delta T_f = -K_f m$

$$T_b - T_f = (100 + K_b m) - (-K_f m)$$

$$105 = 100 + 0.51\text{m} + 1.86\text{ m}$$

$$2.37m = 5 \quad \text{or} \quad m = \frac{5}{2.37} = 2.11$$

$\therefore$ Weight of sucrose to be dissolved in 100 g water

$$= \frac{2.11 \times 342}{1000} \times 100 = 72\text{ g}$$

9. **For cane sugar solution**

W_b (sugar) = 5 g; W_A (water) = 100 − 5 = 95 g

M_B (sugar) = 342 g mol^{-1}; $\Delta T_f = (273.15 - 271.00)$ K

= 2.15 K

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

$$(2.15\text{ K}) = \frac{K_f \times (5\text{ g})}{(342\text{ g mol}^{-1}) \times (95\text{ g})} \qquad \text{....(i)}$$

For glucose solution

W_B (glucose) = 5 g; W_A (water) = 100 − 5 = 95 g

M_B (glucose) = 180 g mol^{-1}; ΔT_f = ?

$$\Delta T_f = \frac{K_f \times (5\text{ g})}{(180\text{ g mol}^{-1}) \times (95\text{ g})} \qquad \text{...(ii)}$$

On dividing Eq. (ii) by Eq. (i)

$$\frac{\Delta T_f}{(2.15\text{ K})} = \frac{K_f \times (5\text{ g})}{(180\text{ g mol}^{-1}) \times (95\text{ g})} \times \frac{(342\text{ g mol}^{-1}) \times (95\text{ g})}{(K_f) \times (5\text{ g})}$$

$$\Delta T_f = \frac{342 \times 2.15}{180}\text{ K} = 4.085\text{ K}$$

Freezing point for 5% glucose solution

$$= (273.15 - 4.085)\text{ K} = 269.07\text{ K}$$

10. For ideal solution, Raoult's law is $p_T = p_A^\circ \chi_A + p_B^\circ \chi_B$

and vapour pressure in vapour phase $= \frac{p_A^\circ \chi_A}{p_T}$

Thus, the required quantities are χ_A, χ_B and p_T as we know p_A° and p_B°.

Molar mass of benzene $(C_6H_6) = 78$ g mol^{-1}

Molar mass of naphthalene $(C_{10}H_8) = 128$ g mol^{-1}

$n_{C_6H_6}$ (Number of moles of benzene)

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

$n_{C_{10}H_8}$ (Number of moles of naphthalene)

$$= \frac{(100\text{ g})}{(128\text{ g mol}^{-1})} = 0.781\text{ mol}$$

Mole fraction of benzene

$$(\chi_{C_6H_6}) = \frac{(1.026\text{ mol})}{(1.026 + 0.781)\text{ mol}} = 0.568$$

Mole fraction of naphthalene $(\chi_{C_{10}H_8}) = 1 - 0.568 = 0.432$

Applying Raoult's law,

Partial vapour pressure of benzene in solution $(p_{C_6H_6})$

$$= p^\circ_{C_6H_6} \times \chi_{C_6H_6}$$

$$= (50.71\text{ mm}) \times (0.568)$$

$$= 28.80\text{ mm}$$

Partial vapour pressure of naphthalene in solution

$$(p_{C_{10}H_8}) = p^\circ_{(C_{10}H_8)} \times \chi_{C_{10}H_8}$$

$$= (32.06\text{ mm}) \times (0.432)$$

$$= 13.85\text{ mm}$$

Total vapour pressure of solution (*p*)

$$= (28.80 + 13.85)\text{ mm}$$

$$= 42.65\text{ mm}$$

Mole fraction of benzene in vapour phase

$$= \frac{\chi_{C_6H_6} \times p^\circ{}_{C_6H_6}}{p_{\text{total}}}$$

$$= \frac{0.568 \times (50.71\text{ mm})}{(42.65\text{ mm})} = 0.675$$

11. Degree of association, $\alpha = \frac{1-i}{1-\frac{1}{n}} \Rightarrow 0.8 = \frac{1-i}{1-\frac{1}{4}}$

$$i = 0.4$$

$$\because \qquad \Delta T = i \times K_f \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{m_B \times 100}$$

$$m_B = \frac{0.4 \times 1.86 \times 2.5 \times 1000}{0.3 \times 100} = 62\text{ g mol}^{-1}$$

12.

$$\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$$

$$1 \times 1 + 3.5V = 2.5\,(1 + V)$$

$$1 + 3.5V = 2.5 + 2.5\,V$$

or $$V = 1.5 \text{ L}$$

13. ***Step* I Calculation of molar mass of the solute**

***Case* I** Number of mole of solute

$$(n_B) = \frac{\text{mass}}{\text{molar mass}} = \frac{(30 \text{ g})}{(M \text{ g mol}^{-1})} = \frac{30}{M} \text{ mol}$$

Number of moles of water

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

Mole fraction of water

$$(\chi_A) = \frac{n_A}{n_A + n_B} = \frac{(5 \text{ mol})}{\left(5 \text{ mol} + \frac{30}{M} \text{ mol}\right)} = \frac{M}{(6 + M)}$$

Vapour pressure of first solution $(p_A) = 2.8$ kPa

According to Raoult's law, $p_A = p_A^\circ \chi_A$

$$(2.8 \text{ kPa}) = p^\circ_A\, x \frac{M}{(6 + M)} \qquad \text{...(i)}$$

***Case* II** Number of moles of solute $(n_B) = \frac{30}{M}$ mol

Number of moles of water

$$(n_A) = \frac{\text{mass}}{\text{molar mass}} = \frac{(108 \text{ g})}{(18 \text{ g mol}^{-1})} = 6 \text{ mol}$$

Mole fraction of water $(\chi_A) = \dfrac{n_A}{n_A + n_B}$

$$= \frac{(6 \text{ mol})}{\left(6 \text{ mol} + \frac{30}{M} \text{ mol}\right)} = \frac{M}{(5 + M)}$$

Vapour pressure of solution $(p_A) = 2.9$ kPa

According to Raoult's law, $p_A = p_A^\circ \chi_A$

$$(2.9 \text{ kPa}) = p_A^\circ \times \frac{M}{(5 + M)} \qquad \text{... (ii)}$$

Dividing Eq. (i) by Eq. (ii)

$$\frac{(2.8 \text{ kPa})}{(2.9 \text{ kPa})} = \frac{(5 + M)}{(6 + M)}$$

$$0.9655 = \frac{(5 + M)}{(6 + M)}$$

$$(0.9655 \times 6) + 0.9655 \text{ M} = 5 + M$$

$$0.0345 \text{ M} = 0.793$$

$$M = \frac{0.793}{0.0345} = 23 \text{ g mol}^{-1}$$

***Step* II Calculation of vapour pressure of water**

According to Raoult's law, $p_A = p_A^\circ \chi_A$

or $$(2.8 \text{ kPa}) = p_A^\circ = \frac{M}{(6 + M)} \qquad \text{...(iii)}$$

Placing the value of M in Eq. (i)

$$2.8 \text{ kPa} = p_A^\circ \frac{(23 \text{ g mol}^{-1})}{(6 + 23) \text{ g mol}^{-1}}$$

$$p_A^\circ = \frac{2.8 \times 29}{23}$$

$$= \frac{81.2}{23} = 3.53 \text{ kPa}$$

14. ***Step* I Calculation of degree of dissociation**

Mass of solute = 10 g

Molar mass of solute

$(\text{CH}_3\text{CH}_2\text{CHClCOOH}) = (12 \times 4) + (1 \times 7) + (35.5) + (16 \times 2)$

$$= 48 + 7 + 35.5 + 32$$

$$= 122.5 \text{ g mol}^{-1}$$

Molal concentration of solution

$$= \frac{\text{mass/molar mass}}{\text{mass of solvent (kg)}}$$

$$= \frac{(10 \text{ g})}{(122.5 \text{ g mol}^{-1}) \times (0.25 \text{ kg})}$$

$$= 0.326 \text{ m}$$

If α is the degree of dissociation of $\text{CH}_3\text{CH}_2\text{CHCl COOH}$, then

$$\text{CH}_3\text{CH}_2\text{CHClCOOH} \rightleftharpoons \text{CH}_3\text{CHClCOO}^- + \text{H}^+$$

Initial conc.	C mol^{-1} kg	0	0
At equilibrium	$C\,(1 - \alpha)$	$C\alpha$	$C\alpha$

$$\therefore \qquad K_a = \frac{C\alpha \times C\alpha}{C\,(1 - \alpha)} = C\alpha^2$$

[Considering $(1 - \alpha) = 1$ for dilute solutions]

$$\alpha^2 = \frac{K_a}{C} \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{C}}$$

So, $$\alpha = \sqrt{\frac{1.4 \times 10^{-3}}{0.326}} = \sqrt{42.9 \times 10^{-4}}$$

$$= 6.55 \times 10^{-2} = 0.065$$

***Step* II Calculation of van't Hoff factor (*i*)**

$$\text{CH}_3\text{CH}_2\text{CHClCOOH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{CHClCOO}^- + \text{H}^+$$

Initial no. of moles	1	0	0
Moles at equilibrium	$1 - \alpha$	α	α

Total number of moles after dissociation

$$= (1 - \alpha) + (\alpha) + (\alpha) = (1 + \alpha)$$

van't Hoff factor

$$(i) = \frac{\text{Total number of moles after dissocation}}{\text{Number of moles before dissocation}}$$

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

***Step* III Calculation of depression in freezing point (ΔT_f)**

$$\Delta T_f = i\,K_f\,m$$

$$= (1.065) \times (1.86 \text{ K kg mol}^{-1}) \times (0.326 \text{ mol kg}^{-1})$$

$$\Delta T_f = 0.65 \text{ K}$$

15. Isotonic solution have same molarity.

$$\text{Molarity of 18 g glucose} = \frac{18}{180}\Big/\frac{1000}{1000} = 0.1$$

$$\text{Molarity of 34.2 g sucrose} = \frac{34.2}{342}\Big/\frac{1000}{1000} = 0.1$$

The concentration of 18 g L^{-1} glucose is same to 34.2 gL^{-1} sucrose.

16. L represents $\Delta T_b = K_b \cdot m$

17. For equimolar solutions $\chi_B = \chi_T = 0.5$

$$p_B = \chi_B \times p_B^\circ = 0.5 \times 160 = 80 \text{ mm}$$

$$p_T = \chi_T \times p_T^\circ = 0.5 \times 60 = 30 \text{ mm}$$

$$p_{\text{total}} = 80 + 30 = 110 \text{ mm}$$

$$\text{Mole fraction of toluene in vapour phase} = \frac{30}{110} = 0.27$$

18. $\Delta T_b = K_b \times m = 0.513 \times 0.69 = 0.354$

$$T_b = T + \Delta T_b = 99.725 + 0.354 = 100.079°\text{C}$$

19. Total mass of solution = 1000 g water + 120 g urea

$$= 1120 \text{ g}$$

Density of solution = 1.15 g/mL

$$\text{Thus, volume of solution} = \frac{\text{mass}}{\text{density}} = \frac{1120 \text{ g}}{1.15 \text{ g / mL}}$$

$$= 973.91 \text{ mL}$$

$$= 0.974 \text{ L}$$

$$\text{Moles of solute} = \frac{120}{60} = 2$$

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume (L) of solution}}$$

$$= \frac{2}{0.974} = 2.05 \text{ mol L}^{-1}$$

20. Coolant is glycol ($C_2H_6O_2$) and is non-electrolyte

$$\Delta T_f = 2.8°$$

$$\Delta T_f = \frac{1000 K_f w_1}{m_1 w_2}$$

$$2.8 = \frac{1000 \times 1.86 \times w_1}{62 \times 1000}$$

$$\therefore \quad w_1 = 93.33 \text{ g}$$

21.

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

$$= \frac{5.2 \text{ mol } CH_3OH}{1 \text{ kg } (= 1000 \text{ g}) \text{ } H_2O}$$

$$n_1(CH_3OH) = 5.2$$

$$n_2(H_2O) = \frac{1000}{18} = 55.56$$

$$\therefore \quad n_1 + n_2 = 5.20 + 55.56 = 60.76 \text{ mol}$$

$$\therefore \quad \chi_{CH_3OH} = \text{Mole fraction of } CH_3OH$$

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

$$= \frac{5.2}{60.76} = 0.086$$

22. (A) $\text{Molarity} = \frac{10.6}{106} \times \frac{1000}{100} = 1 \text{ M}$

(B) $\text{Molarity} = \frac{34.2 \text{ g L}^{-1}}{342 \text{ g mol}^{-1}} = 0.1 \text{ M}$

(C) 9.8% H_2SO_4 means 9.8 g in 100 g of solution.
Volume of solution = 100 / 1.25 = 80 mL.

$$\text{Molarity} = \frac{9.8}{98} \times \frac{1}{80} \times 1000 = 1.24 \text{ M}$$

(D) 20% of ethanol solution means 20 cc ethanol in 100 cc of solution.

Mass of solution = 100 × 0.938 = 93.8 g

Volume of water = 80 cc

Mass of water = 80 g

Mass of 20 cc ethanol = 93.8 − 80 = 13.8 g

$$\text{Molarity} = \frac{13.8}{46} \times \frac{1}{100} \times 100 = 3.0 \text{ M}$$

23.

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$\text{After dissociation} \quad (1-\alpha) \qquad x\alpha \qquad y\alpha$$

$$i = n(A_xB_y) + n(A^{y+}) + n(B^{x-})$$

$$= 1 - \alpha + x\alpha + y\alpha$$

$$= 1 + \alpha(x + y - 1)$$

$$\therefore \quad \alpha = \frac{i - 1}{(x + y - 1)}$$

24. Two solutions are isotonic if their osmotic pressures are equal.

$$\pi_1 = \pi_2$$

$$M_1ST_1 = M_2ST_2$$

(M_1 and M_2 are molarities)

At a given temperature,

$$M_1 = M_2$$

$$\frac{1000w_1}{m_1V_1} = \frac{1000w_2}{m_2V_2} \qquad (V_1 = V_2 = 100 \text{ mL})$$

Cane sugar Unknown

$$\therefore \quad \frac{w_1}{m_1} = \frac{w_2}{m_2}$$

$$\frac{5}{342} = \frac{1}{m_2}$$

$$m_2 = \frac{342}{5} = 68.4 \text{ g mol}^{-1}$$

25. ΔT_f = freezing point of H_2O − freezing point of ethylene glycol solution = 0 − (−6°) = 6°

K_f = 1.86° kg mol^{-1}

w_1 = Mass of ethylene glycol in gram

w_2 = Mass of solvent (H_2O) in grams = 4000 g

m_1 = Molar mass of ethylene glycol = 62 g mol^{-1}

i = van't Hoff factor = 1

(ethylene glycol being non-electrolyte)

$$\Delta T_f = \frac{1000\,K_f\ w_1(i)}{m_1\ w_2}$$

$$\therefore \qquad 6 = \frac{1000 \times 1.86 \times w_1 \times 1}{62 \times 4000}$$

$$w_1 = 800\ \text{g}$$

26. Solubility of NH_4NO_3 increases with temperature but not continuously. Hence, (A) $\rightarrow$ (r).

Solubility of Li_2CO_3 decreases continuously with temperature. Hence, (B) $\rightarrow$ (s).

Solubility of $Na_2SO_4 \cdot 10H_2O$ first increases upto 34.4°C and then decreases. Hence, (C) $\rightarrow$ (q).

Solubility of KCl increases continuously with temperature.

Hence, (D) $\rightarrow$ (p).

27. $\Delta T = iK_f m$

$$(273 - 269.28) = i \times 1.86 \times 1$$

$$3.72 = i \times 1.86$$

$$i = 2$$

$$\alpha = \frac{i-1}{n-1};\ (\alpha = 100\% = 1)$$

$$1 = \frac{2-1}{n-1} \Rightarrow n = 2$$

28. Let $\pi_1 = 200$ mm; $T_1 = 283$, $\pi_1 = 105.3$; $T_2 = 298$

Now, $\qquad \pi = \dfrac{n}{V} RT$

At T_1, $200 = \dfrac{n}{V_1} R \times 283$

At T_2, $50 = \dfrac{n}{V_2} \times R \times 298$

Dividing Eq. (i) by Eq. (ii), we get

$$\frac{200}{105.3} = \frac{V_2}{V_1} \times \frac{283}{298}$$

$$\Rightarrow \qquad V_2 = 2V_1$$

29.

$$\pi = CRT = \frac{\left(\dfrac{W_2}{Mw_2}\right) RT}{V}$$

Given, $W_2 = 40$ g

$Mw_2 = 246$

$T = 27^\circ C = 300$ K

$V = 1$L

Substituting all the values, we get

$$\pi = \frac{40}{246} \times 0.082 \times 300 = 4\ \text{atm}$$

30. $\Delta T_b = iK_b m$

$$0.27 = i \times 0.54 \times \frac{12.2}{122} \times \frac{1000}{100}$$

or $i = 0.5$

Therefore, benzene associated as dimer, i.e. 2.

31. Hardness in ppm

Mass of $CaCO_3$ equivalent to the total number of

$$\text{moles of} = \frac{\text{hardness causing substances} \times 10^6}{\text{Mass of water sample}}$$

Here, $[Mg^{2+}] = 10^{-3}$ M

$$n_{Mg^{2+}} = 10^{-3} \text{ per 1 L water 1000 g}$$

Mass of 10^{-3} mole of $CoCO_3$ $+ 10^{-3} \times 100\ \text{g} = 0.1$ g

$$\text{ppm} = \frac{0.1 \times 10^6}{1000} = 100\ \text{ppm}$$

32. Osmotic pressure,

$$\pi = i \times C \times RT$$

Here, i = van't Hoff factor, T = temperature

C = concentration and R = gas constant.

For NaCl, $i = 2$

So, $\qquad \pi_{NaCl} = i \times C_{NaCl} \times RT$

$$0.1 = 2 \times C_{NaCl} \times RT$$

$$C_{NaCl} = \frac{0.05}{RT}$$

For glucose, $i = 1$ because it cannot ionise

So, $\qquad \pi_{glucose} = i \times C_{glucose} \times RT$

$$0.2 = 1 \times C_{glucose} \times RT$$

$$C_{glucose} = \frac{0.2}{RT}$$

($\because n_{NaCl}$ = numbers of moles NaCl)

n_{NaCl} in 1 L $= C_{NaCl} \times V_{litre}$

$= \dfrac{0.05}{RT}$ ($n_{glucose}$ = number of moles of glucose)

$n_{glucose}$ in 2 L $= C_{glucose} \times V_{litre} = \dfrac{0.4}{RT}$

$$V_{total} = 1 + 2 = 3\text{L}$$

So, final conc. NaCl $= \dfrac{0.05}{3RT}$

Final conc. glucose $= \dfrac{0.4}{3RT}$

$$\pi_{total} = \pi_{NaCl} + \pi_{glucose}$$

$$= [i \times C_{NaCl} + C_{glucose}]\ RT$$

$$= \left(\frac{2 \times 0.05}{3RT} + \frac{0.4}{3RT}\right) \times RT$$

$$= \frac{0.5}{3}\ \text{atm}$$

$$= 0.1666\ \text{atm} = 166.6 \times 10^{-3}\ \text{atm}$$

$$= 167.00 \times 10^{-3}\ \text{atm}$$

So, $\qquad x = 167.00$

33. Most precise volume of HCl = 5 mL at equivalence point

Meq. of Na_2CO_3 = meq. of HCl.

Let molarity of Na_2CO_3 solution = M, then

$$M = 0.05\ \text{mol/L}$$

$$= 0.05 \times 1000 = 50\ \text{mM}$$