# 20. SOLUTIONS AND COLLIGATIVE PROPERTIES

## 1. INTRODUCTION

**(a)** Solutions are homogenous mixtures of two or more substances.

**(b)** We call what is being dissolved in the solution as a "solute": for, it is the active 'ingredient' of that particular solution.

**(c)** In the same way, in what we are dissolving the solute is termed as a "solvent": Typically, there is more solvent than any solute.

**(d)** Further, solutes and solvents can be technically in any state of matter.

Solutions that contain relatively high concentration of a solute are called concentrated solutions, whereas solutions that contain relatively low concentration of a solute are called dilute solutions.

Let us now discuss saturated, unsaturated and supersaturated solutions.

Generally by saturated solution we mean a solution, which contains as much solute as it can hold particularly at a given temperature. Similarly, a solution, which contains comparatively less solute than the quantity of solute it can actually hold is called a unsaturated solution. Further, a solution is called a supersaturated solution, if it contains comparatively more solute than the quantity it can actually hold at a particular temperature.

Binary solutions are such solutions that hold only two components.

We now proceed to discuss various types of solutions.

**Table 20.1:** Types of Solutions

| S. No. | Solute | Solvent | Type of solution | Example |
|---|---|---|---|---|
| SOLID SOLUTIONS (solid solvent) | | | | |
| 1. | Solid | Solid | Solid in solid | Alloy (brass, German silver, bronze, 22 carat gold, etc.) |
| 2. | Liquid | Solid | Liquid in solid | Hydrated salts, amalgam of Hg with Na |
| 3. | Gas | Solid | Gas in solid | Dissolved gases in minerals or $H_2$ in Pd |
| LIQUID SOLUTIONS (liquid solvent) | | | | |
| 4. | Solid | Liquid | Solid in solid | Salt or glucose or sugar or urea solution in water |
| 5. | Liquid | Liquid | Liquid in solid | Methanol or ethanol in water |
| 6. | Gas | Liquid | Gas in solid | Aerated drinks, $O_2$ in water |

| S. No. | Solute | Solvent | Type of solution | Example |
|--------|--------|---------|------------------|---------|
| GASEOUS SOLUTIONS (gaseous solvent) | | | | |
| 7. | Solid | Gas | Solid in Gas | Iodine vapors in air, camphor in $N_2$ gas |
| 8. | Liquid | Gas | Liquid in Gas | Humidity air, chloroform mixed with $N_2$ gas |
| 9. | Gas | Gas | Gas in Gas | Air ($O_2 + N_2$) |

Out of the various types of solutions listed in the table given above, the most significant types of solutions are those which are in liquid phase, i.e., liquid solutions. We therefore confine ourselves to the study of solutions of solids, liquids or gases in liquids.

## 2. METHODS FOR EXPRESSING CONCENTRATION OF SOLUTIONS

**1. Mass percentage:** % (w/w) Mass percentage of solute = $\dfrac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$

**2. Percent mass by volume:** % (w/v) = $\dfrac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$

**3. Volume percentage:** Percent of solute by volume = $\dfrac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$

**4. Percentage mass by volume:** Percent of solute mass by volume = $\dfrac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$

**5. Strength of concentration:**

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

**6. Parts per million (ppm):** = $\dfrac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$

**7. Mole Fraction:** Let us assume that $n$ moles of solute (A) and $N$ moles of solvent (B) are present in a solution.

Then, mole fraction of the solute = $\dfrac{n}{N+n} = X_A$, whereas mole fraction of the solvent = $\dfrac{N}{N+n} = X_B$

Hence, in a binary solution, $X_A + X_B = 1$.

Mole fraction is, therefore, independent of temperature of the solution.

**8. Molality:** Molality (m) = $\dfrac{\text{Number of moles of solute}}{\text{Number of kilograms of the solvent}}$

**9. Molarity:** Molarity (M) = $\dfrac{\text{Number of moles of solute}}{\text{Number of litres of solution}}$

Molarity × Number of liters of solution = Number of mole of solute

**10. Normality:** Normality (N) = $\dfrac{\text{Number of gram equivalents of solute}}{\text{Number of litres of the solution}}$

Or Normality × Number of liters of the solution = Number of gram equivalents of the solute.

## PLANCESS CONCEPTS

**Relation between molality and mole fraction** $\dfrac{X_B \times 1000}{(1 - X_B)m_A} = m$

Molality is the most convenient form of representing concentration of a solution as it is independent of temperature.

**Relation between molality and molarity** $\dfrac{1}{m} = \dfrac{\rho}{M} - \dfrac{m_B}{1000}$

where, $\rho$ = density of solution; m = molality; M = molarity and $m_B$ = molar mass of a solute.

**Relation between molarity and mole fraction** $M = \dfrac{x_B \times 1000 \times d}{x_A m_A + x_B m_B}$

**Relation between normality and strength**

Normality × Equivalent mass = $\dfrac{w_B}{V}$ = Strength of the solution in g/L

**Relation between normality and molarity**

Normality = n × Molarity

If volume $V_1$ of a solution of normality $N_1$ is mixed with volume $V_2$ of another non-reacting solution of normality $N_2$, then the normality $N_3$ of the final solution can be calculated as follows:

$N_1V_1 + N_2V_2 = N_3(V_1 + V_2)$ or $N_3 = (N_1V_1 + N_2V_2) / (V_1 + V_2)$

Similarly, if molarities are used, then $M_3 = (M_1V_1 + M_2V_2) / (V_1 + V_2)$

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**Illustration 1:** The density of a solution containing 13% by mass of sulfuric acid is 1.09 g/mL. Calculate its molarity. **(JEE MAIN)**

**Sol:** We are provided with strength of solution and density hence for this numerical following formula can be applied

In solving such problems, the following formula can be applied:

Molarity = $\dfrac{\%\text{strength of soln.} \times \text{density of soln.} \times 10}{\text{Mol. mass}}$; M = $\dfrac{13 \times 1.09 \times 10}{98}$ = 1.445 M

**Illustration 2:** The density of a 3M sodium thiosulphate solution ($Na_2S_2O_3$) is 1.25 g/mL. Calculate (i) the percentage by mass of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate and (iii) molalities of $Na^+$ and $S_2O_3$ ions. **(JEE ADVANCED)**

**Sol:** From the given data determine the strength of the acid. In order to determine the mole fraction we have to calculate the no of moles of acid and water present in the solution. From the number of moles calculate the molalities of different ions.

$M = \dfrac{x \times d \times 10}{m_A}$ $\Rightarrow 3 = \dfrac{x \times 1.25 \times 10}{158}$ ∴ $x = 37.92$

No. of moles of $Na_2S_2O_3 = \dfrac{474}{158} = 3$; mass of water = $(1250 - 474) = 776$g

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

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

No. of moles of $Na^+$ ion = 2 × No. of moles of $Na_2S_2O_3$ = 2 × 3 = 6

Molality of $Na^+$ ion = $\dfrac{\text{No. of moles of } Na^+ \text{ ions}}{\text{Mass of water in kg}} = \dfrac{6}{776} \times 1000 = 7.73$ m

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

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

## 3. SOLUBILITY

Solubility is defined as the maximum amount of solute that we can dissolve in any given solvent (yielding a saturated solution). It not only depends on the nature of solute and solvent but also on temperature and pressure.

### 3.1 Solubility of a Solid in Liquid

Suppose that a solid solute is added continuously to a liquid solvent; then, the solute continues dissolving and consequently the concentration of the solution increases. We call this process as dissolution. However, ultimately, a state is reached where no more solute dissolves at the given temperature. This is basically because of the fact that from the solution, the solute particles keep on colliding on the surface of solid solute particles and ultimately get separated out of the solution. This process is known as crystallization. Thereafter, no more solute particles dissolve because the rate of dissolution equalizes the rate of crystallization, i.e., a dynamic equilibrium is attained.

Solute + Solvent $\longrightarrow$ Solution

Further, the solution at this stage is said to be a saturated solution. However, an unsaturated solution is one in which more solute particles dissolve at the same temperature. Thus, the concentration of such a saturated solution is called its 'solubility.' Now, as per our discussion so far in this regard, we define solubility as follows:

**The solubility of a solid in a liquid at any temperature is defined as the maximum amount of the solid (solute) in grams which can dissolve in 100g of the liquid (solvent) to form the saturated solution at that particular temperature.**

**Factors affecting solubility of a solid in a liquid**

**(a)** **Nature of Solute and Solvent:** Generally, a solid dissolves in a liquid which is chemically similar to it. We can say this conveniently as 'like dissolves like.' In this regard, ionic compounds usually get dissolved in polar solvents, whereas covalent compounds are soluble in non-polar solvents.

**Explanation:** For ionic compounds that are being dissolved in polar solvents, the solubility is due to the fact that there are strong electrostatic forces of attraction between the ions of the crystal and the polar solvent molecules with the negative ions being attracted with the positive poles of the solvent molecule and positive ions by negative poles. However, in case of water molecule, the situation can be represented as
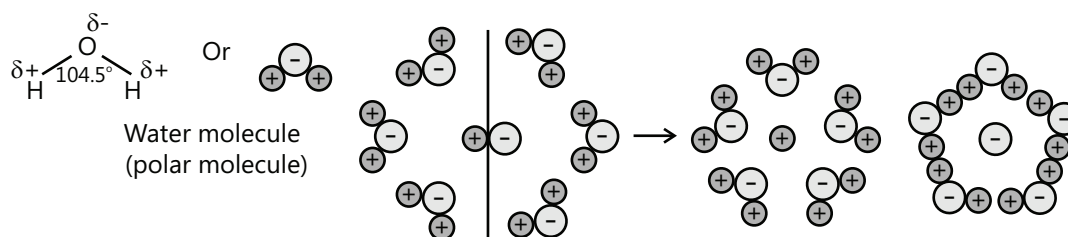


**Figure 20.1:** Dissociation of an ionic compound, like $Na^+Cl^-$, in a polar solvent ($H_2O$)

Thus, the water molecules pull apart the ions of the crystal and the electrostatic forces of attraction between the ions of the crystal are hence cut off. Further, we observe that the ions are surrounded by the water molecules which act as a sheath (or envelope) around the ions and hence prevent the possible recombination of the ions. Such ions that are thus moving freely in the solution are said to be hydrated. It is to be noted here that whereas energy is required for the splitting of the ionic compound into ions (called lattice energy), energy is released when the ions get hydrated (called hydration energy). It follows then that a substance dissolves if its hydration energy is greater than its lattice energy, i.e., $\Delta_{hyd} H > \Delta_{lattice} H$.

It may be further mentioned here that whereas water is the best polar solvent (having the highest dielectric constant), liquid ammonia, liquid hydrogen sulfide and liquid sulfur dioxide are also good solvents for ionic compounds.

In the case of non-polar compounds being dissolved in non-polar solvents, the solubility principle is due to similar solute–solute, solute–solvent and solvent–solvent interactions.

**(b) Temperature:** The solubility of solutes is generally dependent on temperature. For example, when a solid dissolves in a liquid, a change in the physical state of the solid, analogous to melting, takes place. However, heat is required to break the bonds holding the molecules in the solid together. On the contrary, heat is liberated during the formation of new solute–solvent bonds.

## PLANCESS CONCEPTS

Solute + Solvent $\rightarrow$ Solution. $\Delta H_{solution} = \pm x$

If $\Delta H_{solution} < 0$, i.e., (–ve), then the dissolution is exothermic. In this case, as the temperature increases, solubility decreases (Le Chatelier's principle).

If $\Delta H_{solution} > 0$, i.e., (+ve), then there is endothermic dissolution. In this case, increase in temperature increases the solubility (Le Chatelier's principle).

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## 3.2 Solubility of a Gas in a Liquid

The solubility of any gas in a particular liquid is the volume of the gas in cc (converted to STP) that can dissolve in unit volume (1 cc) of the liquid to form the saturated solution at the temperature of the experiment and under a pressure of one atmosphere. This method helps us to express the concentration as an absorption coefficient of the gas and is usually represent by $\alpha$.

Further, solubility of a gas in a liquid at a particular temperature is also expressed in terms of **molarity** (moles of the gas dissolved per liter of the solvent to form the saturated solution, i.e., in terms of mol $L^{-1}$) or in terms of **mole fraction** ($x_A$) of the gas.

**(a) Nature of the gas and solvent:** It is to be noted here that gases like $H_2$, $O_2$, $N_2$, etc. dissolve in water only to a small extent, whereas gases such as $CO_2$, HCl and $NH_3$ are highly soluble. However, the greater solubility pattern of the latter gases is mainly due to their reaction with the solvent or chemical similarity.

**(b) Effect of Temperature:** The solubility nature of gases decreases with an increase in temperature as dissolution is an exothermic process, i.e., it is accompanied by evolution of heat. Thus

Gas + Solvent $\longrightarrow$ Solution + Heat
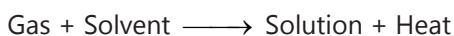
By applying Le Chatelier's principle, it is clearly evident that increase of temperature would shift the equilibrium in the backward direction, i.e., the solubility would decrease.

**Exceptions –** The solubility of some sparingly soluble gases, such as hydrogen and inert gases, increases slightly with increase of temperature especially in the case of non-aqueous solvents such as hydrocarbons, alcohols and acetone.

**(c) Effect of Pressure (Henry's law):** As the pressure increases, the solubility also increases. We explain this concept using the following example. As an example of a solution of a gas in a liquid, consider a system as shown in Fig. 2 (a). In this figure, the lower part is the solution, whereas the upper part is gaseous at pressure p and temperature T. Now, let us suppose that the system is in dynamic equilibrium, i.e., rate of gaseous particles entering and leaving the solution is the same, which means that rate of dissolution = rate of evaporation. Now, let us increase the pressure over the system as shown in Fig. 2 (b). Consequently, the gas gets compressed to a smaller volume. Due to this effect, the total number of gaseous particles per unit volume tends to increase. Because of this, the total number of gaseous particles striking at the surface of the solution and hence entering into it also increases. The process is continuous till a new equilibrium is reestablished. Thus, we learn that upon increase of the pressure of the gas above the solution, the solubility also increases.
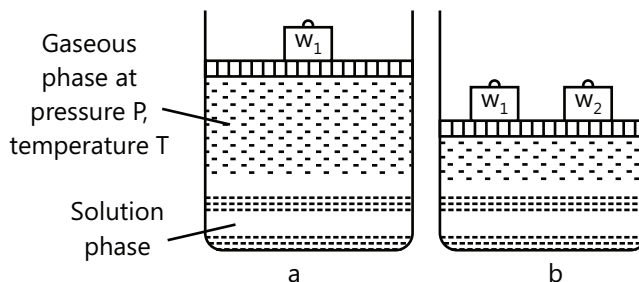


**Figure 20.2:** Demonstrating the effect pressure on solubility of a gas in liquid

Quantitatively, this fact was also explained by Henry's law which states that the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution at a definite temperature.

$m \propto P$ or $m = Kp$

In this regard, Dalton also concluded independently that, if a mixture of gases is simultaneously is in equilibrium with the liquid at a particular temperature, then the solubility of any gas in the mixture is directly proportional to the partial pressure of that gas in the mixture.

By expressing solubility in terms of mole fraction of the gas in the solution, for a gas A, Henry's law can be written as $X_A = K'P_A$

However, this can also be written as: $P_A = \dfrac{1}{K'} X_A$ or $P_A = K_H X_A$ where, $K_H = \dfrac{1}{K'}$ is called Henry's constant.

**Limitations of Henry's law**

Henry's law is applicable only when

The pressure of the gas is not too high and temperature is not too low.

The gas should not undergo any chemical change.

The gas should not undergo association or dissociation in the solution.

**Illustration 3:** Why sealed soda water bottle upon opening shows the evolution of gas with effervescences?

**(JEE MAIN)**

**Sol:** $CO_2$ gas is dissolved at high pressure in soda water bottle. On opening the seal, pressure becomes equal to atmospheric pressure and the dissolved gas comes out from solution with effervescences because solubility of gas decreases with decrease in pressure.

**Illustration 4:** $NH_3$ is one of the few gases that do not obey Henry's law. Suggest a reason.  **(JEE ADVANCED)**

**Sol:** The solubility of $NH_3$ in water also involves H-bonding and thus, solubility of $NH_3$ in water depends on pressure as well as tendency to show H-bonding.

## PLANCESS CONCEPTS

Calculation of solubility of a gas at a particular pressure from the known solubility at some other pressure (but at the same temperature).

From Henry's law, we know that m = Kp. Hence, if $m_1$ is the solubility of a gas at pressure $P_1$ and $m_2$ is its

solubility at pressure $P_2$, then $\dfrac{m_1}{m_2} = \dfrac{P_1}{P_2}$.

Thus, by knowing $m_1$ at $P_1$, we can easily calculate $m_2$ at $P_2$. Further, the equation, m = KP also suggests that the plot of pressure P vs. solubility m will be a straight line passing through the origin with slope = K. However, the greater the value of K, the greater is the solubility. For example, $O_2$ is more soluble than $N_2$ at the same temperature and pressure as shown in the figure provided.

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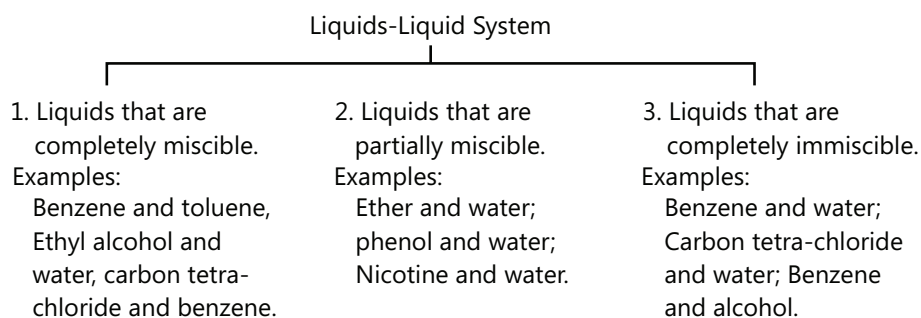
## 3.3 Solutions of Liquids in Liquids

Consider the case wherein one liquid dissolves in another. Here, the molecules of the solvent are forced to move apart so as to accommodate the solute molecules. In the same way, the molecules in the solute must also be separated so that they can assume their positions in the mixture. However, it is to be noted here that in both these processes, energy is required. Further, as the molecules of both the solute and the solvent are brought together, there is release of energy due to the attractive forces between them. Moreover, when the molecules of both the solute and the solvent are strongly attracted to each other, more energy is released in the final step. There is a possibility of three cases under such circumstances. Either the overall dissolution process results in evolution of heat or absorption of heat, or energy is released in the final step of the reaction and is the same as the energy absorbed in the first two phases, i.e., net change is zero.

**Examples**

1. Benzene and carbon tetrachloride          No evolution or absorption of heat

2. Acetone and water                          Evolution of heat

3. Ethyl alcohol and water                    Absorption of heat

However, we must be aware of the fact that a liquid may or may not be soluble in another liquid. Therefore, purely based upon the relative solubility of a liquid in another, the following three cases are possible:

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

Liquids-Liquid System

| 1. Liquids that are completely miscible. Examples: Benzene and toluene, Ethyl alcohol and water, carbon tetra-chloride and benzene. | 2. Liquids that are partially miscible. Examples: Ether and water; phenol and water; Nicotine and water. | 3. Liquids that are completely immiscible. Examples: Benzene and water; Carbon tetra-chloride and water; Benzene and alcohol. |
|---|---|---|

**Flowchart 20.1:** Types of liquid-liquid system

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

# 4. IDEAL SOLUTION AND RAOULT'S LAW

## 4.1 Ideal Solution

By an ideal solution, we mean the one that obeys Raoult's law (we discuss this law hereunder) for a wide range of concentrations and at a specified temperature. Some examples in this regard include

(1) Mixture of methanol and ethanol;

(2) Mixture of n-hexane and n-heptane and

(3) Mixture of benzene and toluene.

### Characteristics

**(a)**  Volume change on mixing should be zero, i.e., $\Delta V_{mix} = 0$;  $V_{Solvent} + V_{solute} = V_{solution}$

**(b)**  Heat change on mixing should be zero, i.e., $\Delta H_{mix} = 0$ (heat is neither absorbed nor evolved)

**(c)**  Solute must not undergo association or disociation in solution

**(d)**  There should be no chemical reaction between the solute and solvent

### Things to remember

**(a)**  If $F_{A-A}$ is the force of attraction between molecules of A and $F_{B-B}$ is that of molecules of B, then A and B will form an ideal solution only if, $F_{A-B} = F_{A-A} = F_{B-B}$.

**(b)**  The solution of liquids A and B will be ideal if A and B have similar structures. Further, both methanol and ethanol have the same functional group and almost same polarity and therefore, form ideal solutions.

## 4.2 Non-Ideal Solution

A solution which does not obey Raoult's law is called a non-ideal solution.

For a non-ideal solution.

**(a)**  Raoult's law is not obeyed, i.e., $P_A \neq P_A^0 x_A$ and $P_B \neq P_B^0 x_B$.

**(b)**  $\Delta H_{mix} \neq 0$ and

**(c)**  $\Delta V_{mix} \neq 0$

## 4.3 Raoult's Law

This law states that the partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.

Let us assume that a mixture is prepared containing $n_A$ and $n_B$ moles of liquid A and B, respectively. Further, let $P_A$ and $P_B$ be the partial pressures of A and B, respectively and $P_A^0$ and $P_B^0$ the vapour pressure pure state.

Thus, according to Raoult's law,

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

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

If the total pressure be P, then

$$P = P_A + P_B = \frac{n_A}{n_A + n_B} P_A^o + \frac{n_B}{n_A + n_B} P_B^o \quad \text{Thus,} \qquad P = X_A P_A^0 + X_B P_B^0$$

## 4.4 Ideal and Non-Ideal Solutions

**Table 20.2:** Differences between ideal and non-ideal solutions

| Ideal solutions | Non-ideal solutions | |
|---|---|---|
| | **Positive deviation from Raoult's law** | **Negative deviation from Raoult's law** |
| 1. Obey Raoult's law at every range of concentration | Do not obey Raoult's law | Do not obey Raoult's law |
| 2. $\Delta H_{mix} = 0$; neither heat is evolved nor absorbed during dissolution | $\Delta H_{mix} > 0$; endothermic dissolution; heat is absorbed | $\Delta H_{mix} < 0$; exothermic dissolution; heat is evolved |
| 3. $\Delta V_{mix} = 0$; total volume of solution is equal to sum of volumes of the components | $\Delta V_{mix} > 0$; volume is increased after dissolution | $\Delta V_{mix} < 0$; volume is decreased during dissolution |
| 4. $P = P_A + P_B = P_A^0 X_A + P_B^0 X_B$ i.e., $P_A = P_A^0 X_A$; $P_B = P_B^0 X_B$ | $P_A > P_A^0 X_A$; $P_B > P_B^0 X_B$ $\therefore P_A + P_B > P_A^0 X_A + P_B^0 X_B$ | $P_A < P_A^0 X_A$; $P_B < P_B^0 X_B$ $\therefore P_A + P_B < P_A^0 X_A + P_B^0 X_B$ |
| 5. A – A, A – B, B – B interactions should be same, i.e., 'A' and 'B' are identical in shape, size and character | A – B attractive force should be weaker than A – A and B – B attractive forces. 'A' and 'B' have different shape, size and character. | A – B attractive force should be greater than A – A and B – B attractive forces. 'A' and 'B' have different shape, size and character. |
| 6. Escaping tendency of 'A' and 'B' should be the same in pure liquid and in the solution | 'A' and 'B' escape easily showing higher vapor pressure than the expected value | Escaping tendency of both components 'A' and 'B' is lowered showing lower vapor pressure than expected ideally |
| **Examples** Dilute solutions; benzene + toluene | **Examples** Acetone + ethanol; acetone + CS$_2$ | **Examples** Acetone + aniline; acetone+ chloroform |

## 4.5 Relation Between Dalton's Law and Raoult's Law

In this regard, we can calculate the composition of the vapour in equilibrium with the solution by applying Dalton's law of partial pressures. Let us assume that the mole fractions of vapours A and B be $Y_A$ and $Y_B$ respectively. Further, let $P_A$ and $P_B$ be the partial pressures of vapours A and B, respectively and the total pressure be P.

$$P_A = Y_A P \qquad \qquad \text{...(i)}$$

$$P_B = Y_B P \qquad \qquad \text{...(ii)}$$

$$P_A = X_A P_A^0 \qquad \qquad \text{...(iii)}$$

$$P_B = X_B P_B^0 \qquad \qquad \text{...(iv)}$$

Now, by equating (i) and (iii), we obtain

$$Y_A P = X_A P_A^0 \quad \text{or} \quad Y_A = \frac{X_A P_A^0}{P} = \frac{P_A}{P}$$

Similarly, by equating (ii) and (iv), we obtain $Y_B = \frac{X_B P_B^0}{P} = \frac{P_B}{P}$ .

Thus, it is clear to us that in the case of an ideal solution the vapor phase is richer with more volatile component, i.e., the one having relatively greater vapor pressure.

**Illustration 5:** At 300 K, the vapor pressure of an ideal solution containing one mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one mole B is added to this solution, the vapor pressure of solution increases by 10 mm of Hg. Calculate the VP of A and B in their pure state. **(JEE MAIN)**

**Sol:** $\because P_M^0 = P_A^0 \cdot X_A + P_B^0 \cdot X_B$ (from Raoult's law)

**Case I:** $550 = P_A^0 \times \left[ \frac{1}{1+3} \right] + P_B^0 \left[ \frac{3}{1+3} \right]$ ... (i)

**Case II:** On addition of one mole of B in liquid mixture $560 = P_A^0 \times \left[ \frac{1}{1+4} \right] + P_B^0 \left[ \frac{4}{1+4} \right]$ ... (ii)

Solving eqs. (i) and (ii) $P_A^0 = 400$ mm, $P_B^0 = 600$ mm

**Illustration 6:** The vapor pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg, respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour presure of the solution and the mole fraction of methanol in the vapor. **(JEE ADVANCED)**

**Sol:** Total vapour pressure is a sum of of partail preesure of A and B and partial pressure is given by product of mole fraction and vapour pressure in pure form of A and B. So first we have to find out the mole fraction of A and B and than partial pressure of A and B.

Mole fraction of a compound in the vapour is given by Partial pressure of that compound divided by total vapour pressure of the solution.

Mol. mass of ethyl alcohol = $C_2H_5OH$ = 46; No. of moles of methyl alcohol = $\frac{60}{46}$ = 1.304

Mol. mass of methyl alcohol = $CH_3OH$ = 32; No. of moles of methyl alcohol = $\frac{40}{32}$ = 1.25

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

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

Partial pressure of ethyl alcohol = $X_A \cdot P_A^0$ = 0.5107 × 44.5 = 22.73 mm Hg

Partial pressure of methyl alcohol = $X_B \cdot P_B^0$ = 0.4893 × 88.7 = 43.40 mm Hg

Total vapour pressure of solution = 22.763 + 43.40 = 66.13 mm Hg

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

# 5. THEORY OF FRACTIONAL DISTILLATION

Fractional distillation is the process of separation of one liquid from another (binary mixture) having different boiling points by distillation. However, the information regarding can a particular solution of two liquids can be separated by distillation or not, is provided by the study of liquid–vapor equilibrium diagrams at constant pressure, say, e.g., atmospheric pressure. The separation is possible only when the vapor phase has a composition different from that of the boiling liquid mixture.

## 5.1 Azeotropes and Azeotropic mixture

Azeotropes are binary mixtures having the same composition both in liquid and vapor phase and boil at a constant temperature.

**Types of Azeotropes**

**Minimum Boiling Azeotropes:** These are the binary mixtures whose boiling point is less than either of their two components. The non-ideal solutions show a large positive deviation from Raoult's law for minimum boiling azeotrope at a specific composition, e.g., a mixture of 94.5% ethyl alcohol and 4.5% water by volume.

**Maximum boiling Azeotropes:** These are the binary mixtures whose boiling point is more than either of their two components. The solutions show large negative deviation from Raoult's law for maximum boiling azeotrope at a specific composition, e.g., a mixture of 68% $HNO_3$ and 32% $H_2O$ by mass.

## 5.2 Liquid Solutions of Type I (Ideal Solutions)

If a solution of composition x is heated, then

**(a)** Vapor phase will be richer in B and A will have a composition $x_1$ in the distillate, whereas the residue will become richer in A and let it have a composition y.

**(b)** Now, if this liquid is heated again, the residue will be even more richer in A and if this process is repeated sufficient number of times, then pure A will be obtained from the residue.

**(c)** Similarly, if the distillate is recondensed and then heated again, then the distillate will be richer in B and on continuing the process, pure B will be obtained from the distillate.

**(d)** Thus, we can separate two liquids that form an ideal solution by fractional distillation.
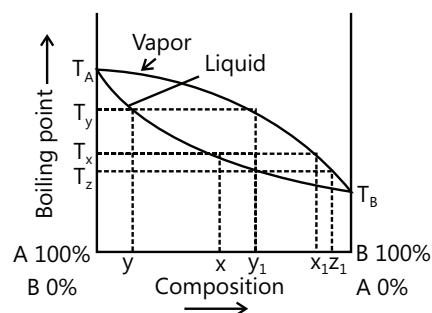


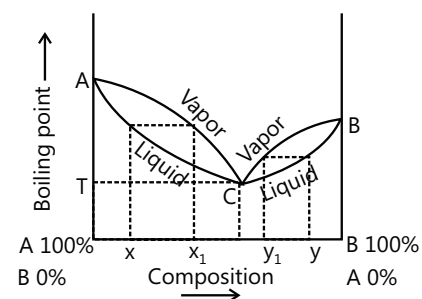**Figure 20.3 a:** Composition of solution showing idea behavior

## 5.3 Type II Solutions (Positive Deviations from Raoult's Law)

If a mixture of composition x is heated, then

**(a)** Vapor will have a composition $x_1$ and the composition of residual liquid will shift toward A while the composition of distillate shifting toward C

**(b)** On repeating fractional distillation, pure liquid A is obtained as a residue while mixture of composition C (minimum boiling azeotropic mixture) is obtained as a distillate.

**(c)** However, pure B cannot be obtained.

If a mixture of composition y is heated, then

**(i)** Vapor will have composition $y_1$ and residual liquid composition will shift toward C.

**(ii)** Ultimately, mixture of composition C is obtained as a distillate and pure liquid B is obtained as A residue

**(iii)** However, it is not possible to obtain pure liquid A.



**Figure 20.3 b:** Composition of solution showing positive deviation from raoults law

## 5.4 Type III Solutions (Negative Deviations from Raoult's Law)

When a mixture composition 'a' is taken, then on boiling

**(a)** Distillate 'a' is obtained, which is richer in component A

**(b)** Residue hence obtained is 'b.' Further, successive distillation of 'b' leads to azeotropic solution D (+ve boiling azeotropic mixture).

**(c)** Successive distillation of 'a' will lead to pure (A).

When a mixture composition 'c' is taken and boiled, then

- **(i)** Distillate obtained is 'c', which is richer in component B and successive distillation of distillates leads to solution becoming pure 'b.'

- **(ii)** The residue of 'c' is 'e.' Further, successive distillation of 'e' makes the residue richer in 'D' which is +ve boiling azeotropic mixture.
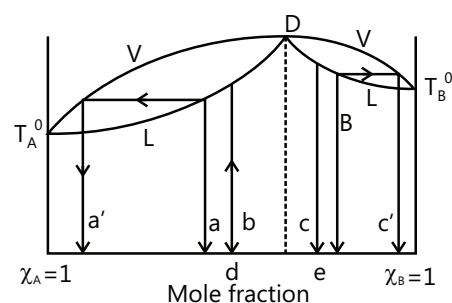


**Figure 20.3 c:** Mole fraction of solution showing negative deviation from raoults law

# 6. COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent.

A dilute solution containing non-volatile solute exhibits some special properties which depends only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as colligative properties and are listed hereunder.

1. Lowering in the vapor pressure,

2. Elevation in the boiling point,

3. Depression in the freezing point and osmotic pressure.

4. Osmotic pressure.

Further, dilute solutions also obey Raoult's law.

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### PLANCESS CONCEPTS

- For applying the formulae of colligative properties, the following conditions should be satisfied:
- The solution should be very dilute.
- The solute should be nonvolatile.
- The solute does not dissociate or associate in solution.

**Vaibhav Krishnan (JEE 2009, AIR 22)**

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## 6.1 Lowering in the Vapor Pressure

When a non-volatile solute is present in a solution, then the vapor pressure of the solution will be less than the vapor pressure of pure solvent.

The vapor pressure may be lowered due to the reasons listed hereunder.

**(a)** Percentage surface area occupied by the solvent decreases. Thus, the rate of evaporation and vapor pressure decreases. The solute molecules occupy the surface, and therefore the percent surface area occupied by the solvent decreases.

**(b)** According to Graham's law of evaporation, rate of evaporation $\propto \dfrac{1}{\sqrt{\text{density}}}$

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

**Now, let us consider the case in detail.**

Let there be a solution of solute B in solvent A.

Since 'B' is nonvolatile, it would not go to the vapor phase; hence, the vapors above the solution will be only due to volatile solvent 'A.' Since



**Figure 20.4:** Lowering in the Vapor Pressure

$P_A = \chi_A P_A^0 \Rightarrow P_A < P_A^0$ so vapor pressure is lowered.

For a binary system, $\chi_A + \chi_B = 1$.

Substituting the value of $\chi_A$

$\Rightarrow P_A = P_A^0(1 - \chi_B); P_A = P_A^0 - P_A{}^o\chi_B$

$\Rightarrow P_A^0 \chi_B = P_A^0 - P = \Delta P$ (relative lowering in vapor pressure); $\Delta P = P_A^0 \chi_B \Rightarrow \Delta P \propto x_B$

$\Rightarrow$ Lowering in vapor pressure is directly proportional to the mole fraction of a solute. Further, the relative lowering in vapor pressure is equal to the mole fraction of solute.

$\dfrac{\Delta P}{P_A^0} = \chi_B$, which can also be written as: $\dfrac{P_A^0 - P}{P_A^0} = \dfrac{n_B}{n_A + n_B}$

or    we can rephrase it as ,

according to Raoult's law, $\dfrac{P_0 - P_s}{P_0} = \dfrac{n_B}{n_B + n_A}$

where, $P_0$ = vapor pressure of pure solvent; $P_s$ = vapor pressure of solution;

$n_2$ = number of moles of solute; and $n_1$ = number of moles of solvent.

## PLANCESS CONCEPTS

- Lowering in vapor pressure is directly proportional to the mole fraction of solute in the solution.

- Relative lowering in vapor pressure is equal to the mole fraction of solute.

- Determination of molecular mass from lowering of vapor pressure.

**Neeraj Toshniwal (JEE 2009, AIR 21)**

We know that, according to Raoult's law, $\dfrac{P^o - P_s}{P^o} = \dfrac{n_B}{n_B + n_A}$ .

If $W_2$ g of the solute is dissolved in $W_1$ g of the solvent and if $M_2$ and $M_1$ are their respective molecular masses, then we have $n_B = \dfrac{w_B}{M_A}$ and $n_A = \dfrac{w_A}{M_A}$ .

By substituting these values in the above expression, we obtain

$$\dfrac{P^o - P_s}{P^o} = \dfrac{w_B / M_B}{w_A / M_A + w_B / M_B} \qquad \qquad \dots \text{(i)}$$

However, for a dilute solution, $n_2$ can be neglected in comparison with $n_1$ so that Raoult's law equation becomes

$$\dfrac{P^o - P_s}{P^o} \equiv \dfrac{n_B}{n_A} \quad \text{or} \quad \dfrac{P^o - P_s}{P^o} \equiv \dfrac{w_B / M_B}{w_A / M_A} \quad \text{or} \quad \dfrac{P^o - P_s}{P^o} = \dfrac{w_B \times M_A}{w_A \times M_B}$$

From expressions (i) and (ii), it is clear that if $w_2$ g of the non-volatile solute is dissolved in $w_1$ g of the solvent and the vapor pressure of the pure solvent ($P^o$) and that of the solution ($P_s$) are measured experimentally, then by knowing the molecular mass of the solvent ($M_1$), that of the solute ($M_2$) can be calculated.

Actually, this is not a preferred method because other methods (namely, elevation in boiling point or depression in freezing point) give results more easily and accurately.

### Determination of Relative Lowering in Vapor Pressure

We can determine the relative lowering in vapor pressure by using Ostwald and Walker method. In this method, a stream of dry air is passed successively through a set of weighed bulbs containing the solution and then through a set of merged bulbs containing pure solvent and finally through weighed U-shaped tubes containing anhydrous $CaCl_2$.

$$\frac{u^2 + Rg}{3g} < \frac{u^2}{2g}$$

(a) Let the loss in weight of solution bulbs be $w_1$ gm

(b) Loss in weight of solvent bulbs be $w_2$ gm

(c) Loss in weight of the solution bulbs ($w_1$) $\propto$ vapor pressure of the solution

(d) Loss in weight of the solvent bulbs ($w_2$) $\propto$ vapor pressure of the solvent – vapor pressure of the solution.

$\Rightarrow P_s \propto w_1$ and $(P_0 - P_s) \propto w_2$

$$\Rightarrow \frac{P^0 - P_s}{P^0} = \frac{w_2}{w_1 + w_2} = \frac{\text{Loss in weight of solvent bulbs}}{\text{Total loss in weight of soltuion bulbs and solvent bulbs}} = X_B$$

i.e., mole fraction of the solute.

### Vapor Pressure of Liquid and Temperature

Liquid $\rightleftharpoons$ Vapor    $\Delta H_{vap} > 0$

Basically, vapor pressure of liquid increases with temperature. Here, $\Delta H$ is enthalpy of vaporization. We provide a graphical representation of vapor pressure versus temperature hereunder.
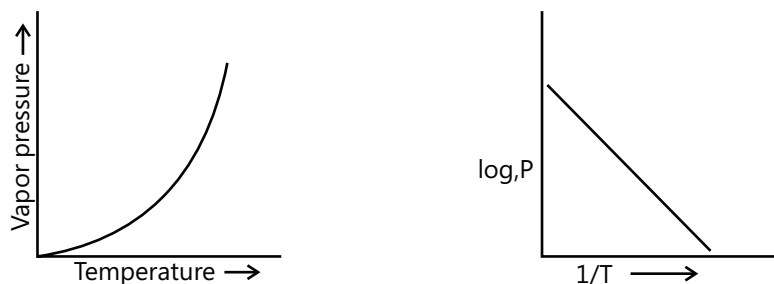


**Figure 20.5:** Variation of vapor pressure with temperature

Generally, if vapor pressure of a liquid is known at a temperature, then it can be calculated at another temperature

using Clausius–Clapeyron equation: $\log_{10}\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap.}}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

Here, $P_1$ = vapor pressure at temperature $T_1$ and $P_2$ = vapor pressure at temperature $T_2$.

## 6.2 Elevation in Boiling Point (Ebullioscopy)

We know that the boiling point of a liquid is the temperature at which its vapor pressure is equal to the atmospheric pressure. Further, the vapour pressure of a liquid is generally lowered upon addition of a non-volatile solute to it. Hence, the temperature of the solution when its vapor pressure will be equal to atmospheric pressure will be higher than the temperature of the pure solvent. In other words, we mean that the boiling point of the solvent is elevated by the addtion of a non-volatile solute. However, the difference in the boiling point of the solution and the boiling point of the pure solvent is termed as **elevation of the boiling point**.

Elevation of boiling point, ($\Delta$T) = Boiling point of the solution – Boiling point of pure solvent

This can be better understood by ploting a graph of vapor pressure vs. temperature for a pure solvent and two solutions of different concentrations. In such a graph, the curves for solution will always lie below the curves for pure solvent.

In the graph provided hereunder, $P^0E$ represents atmospheric pressure, $T_B^0$, $T_1$ and $T_2$ are boiling points for pure solvent, solution-1 and solution-2, respectively. Similarly, the vapor pressures of solution-1 , solution-2 and pure solvent at temperatures $T_B^0$ are $P_1$, $P_2$ and $P^0$, respectively.

Relationship for elevation in boiling points.
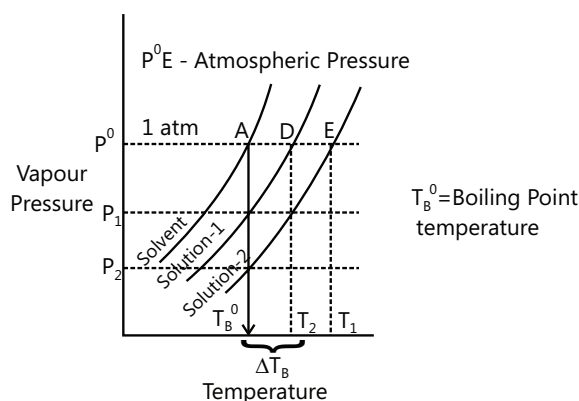


**Figure 20.6:** Elevation in Boiling Point

Let us consider the graph of vapor pressure vs. temperature (in Kelvin scale). Here, triangle ADB and ACE are similar. Hence,

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

$$\frac{T_1 - T^0}{T_2 - T^0} = \frac{P^0 - P_1}{P^0 - P_2} \Rightarrow T_1 - T^0 \propto P^0 - P_1$$

$$\Rightarrow \Delta T_B \propto \Delta P. \text{ Also, } \Delta P \propto X_B \Rightarrow \Delta T_B \propto X_B$$

$$\Delta T_B \propto \frac{n_B}{n_A + n_B} ; \Delta T_B \propto \frac{n_B}{n_A} \text{ [dilute solutions]}$$

$$\Delta T_B \propto \frac{W_B}{M_B} \times \frac{M_A}{W_A} \Rightarrow \Delta T_B = K_b \frac{W_B}{M_B \times W_A}$$

When $\dfrac{W_B}{M_B}$ = 1 mole and $W_A$ = mass of solute in kilogram (kg)

$$\Rightarrow \quad \Delta T_B = K_b \times m \quad m = \text{molality of solution, } K_b = \text{ebullioscopic constant}$$

$$\Delta T_B \propto K_b \quad \text{[when concentration is kept constant].}$$

Hence, elevation in boiling point depends upon $K_B$, i.e., nature of solvent.

$$\Delta T_B \propto m \quad \text{[when solvent taken is same]}$$

$K_b$ is defined as the elevation in boiling point of a solvent when 1-g mole of a non-volatile solute is dissolved in 1000 g of solvent.

$$K_b = \frac{RT_b^2}{1000 \, lv} \quad 1v = \text{latent heat of vaporization per gram of the solvent.}$$

Also, $K_b = \dfrac{RT_b^2 \times M_0}{1000 \times \Delta H_v}$ where $M_0$ = molecular weight of solvent

## PLANCESS CONCEPTS

$$\Delta T_B = \frac{K_b W_{solute}}{M_{solute} \times W_{solvent}} \times 1000 \quad \Delta T_B = \frac{K_b W_B}{M_B \times W_A} \times 1000$$

$W_B = W_{solute}$ = Mass of solute taken

$M_B = M_{solute}$ = Molecular weight of solute

$W_A = W_{solvent}$ = Mass of solvent taken in grams

$$\Rightarrow \quad M_{solute} = \frac{K_b W_B}{\Delta T_B \times W_A} \times 1000$$

Also, $\quad \dfrac{T_{B(1)}}{\Delta T_{B(2)}} = \dfrac{K_{b(1)}}{K_{b(2)}}$ when concentration is same but solvent different

$\dfrac{\Delta T_{B(1)}}{\Delta T_{B(2)}} = \dfrac{m_1}{m_2}$ when solvent is same but concentration different

$\dfrac{\Delta T_{B(1)}}{\Delta T_{B(2)}} = \dfrac{M_{B(2)}}{M_{B(1)}} \Rightarrow \Delta T_B \propto \dfrac{1}{M_{B(1)}}$ when solvent and amount of solute is same

**B Rajiv Reddy (JEE 2012, AIR 11)**

## 6.3 Depression in Freezing Point (Cryoscopy)

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

Depression of freezing point ($\Delta T$) = Freezing point of the solvent – Freezing point of the solution

Here again,

$\Delta T_f \propto \Delta P$

$\Delta P \propto$ molality   or   $\Delta P \propto X_B$

$\Delta T_f \propto$ molality $\qquad \Delta T_f \propto X_B \quad \Rightarrow \Delta T_f \propto \dfrac{n_B}{n_A}$ for dilute solutions

$\Rightarrow \Delta T_f = K_f \dfrac{W_B}{M_B W_A}$ when $W_A$ is in kilogram $\Rightarrow \Delta T_f = K_f m$

$K_f$ = molal depression constant or Cryoscopic constant.

$K_f$ is defined as the depression in freezing point of a solvent when 1 g mole of a non-volatile solute is dissolved

in 1000 g of solvent, i.e., $K_f = \dfrac{RT_f^2}{1000 l_f}$ also $K_f = \dfrac{RT_f^2 M_0}{1000 \Delta H_f}$

where $\quad T_f$ = freezing point and $T_f$ = latent heat of fusion per gram

Also, $\Delta T_f = \dfrac{RT_f \times w_{solute}}{M_{solute} \times W_{solvent}} \times 1000$

Hence, molecular weight of solute

$M_{solvent} = \dfrac{K_f \times W_{solute}}{\Delta T_f \times W_{solvent}} \times 1000$

Since $\Delta T_f = K_f m \Rightarrow \Delta T_f \propto K_f$ [when concentration is same but different solvents are taken]

$\Delta T_f \propto m$ [when solvent is same but different concentration are taken]

## 6.4 Osmotic pressure

**Semipermeable Membrane:** We define a semipermeable membrane as "A membrane which allows the solvent's molecules to pass through it but prevents the passage of solute molecules through it."

**Osmosis:** The phenomenon of osmosis was first observed by Abbe Nollet. It may be defined as a process in which pure solvent molecules pass through a semipermeable membrane from a solution of low concentration to a solution of higher concentration.

(a) Further, exosmosis is the mechanism of outward flow of water from a cell containing an aqueous solution through a semipermeable membrane, e.g., grapes in NaCl solution.

(b) On the other hand, endosmosis is the mechanism of inward flow of water into a cell containing an aqueous solution through a semipermeable mebrane, e.g., grapes in water.

Therefore, if the solution of density d rises to height h, then osmotic pressure is expressed as

$\pi = h \times d \times g,$   where g is the acceleration due to gravity.

Osmotic pressure may also be defined as the excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semipermeable membrane.

However, we can define osmotic pressure in several other ways also as listed hereunder.

**(a)** Osmotic pressure is the excess pressure which must be applied to a given solution in order to increase its vapour pressure until it becomes equal to that of the solution.

**(b)** Osmotic pressure is the negative pressure when a solution is separated from the solvent by a semipermeable membrane.

**(c)** Osmotic pressure is the hydrostatic pressure produced when a solution is separted from the solvent by a semipermeable membrane.

### Differences between Osmosis and Diffusion

Let us now proceed to understand the differences between the processes of osmosis and diffusion as listed hereunder.

**(a)** In the process of diffusion, both the solute as well as the solvent molecules flow in opposite directions while in the process of osmosis the flow of solvent molecules is unidirectional.

**(b)** For osmosis to take place, a semipermeable membrane is essential while it is not so for diffusion.

## 6.4.1 Van't Hoff Theory of Dilute Solutions

Dilute solutions behave like ideal gases and gas laws obeyed by ideal gases are also obeyed by dilute solutions.

We know that

$V \propto \dfrac{1}{\pi}$     (Boyle–van't Hoff law);     $V \propto T$      (Charles–van't Hoff law)

$V \propto n$      (Avogadro–van't Hoff law)

$\Rightarrow$    $V \propto \dfrac{n \times T}{\pi} \Rightarrow$    $V = \dfrac{nRT}{\pi}$       R = solution constant (0.0821 it atm K$^{-1}$ mol$^{-1}$)

$\Rightarrow$    $\pi = \dfrac{n}{V} RT \Rightarrow$    $\pi = CRT$

Hence, at a given temperature, $\pi \propto C$

**Pressure–Temperature law (Gay-Lussac–van't Hoff law)**

Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T), i.e., $\pi \propto T$

or $\quad \dfrac{\pi}{T}$ = constant $\:$ or $\quad \dfrac{\pi}{T}$ = constant

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### PLANCESS CONCEPTS

- $\pi V = nRT$ or $\pi V = nST$ or $\pi = \dfrac{n}{V} ST$ or $\pi = CST$

  where $\pi$ = osmotic pressure in atmospheres

  n = number of moles of the solute present in V liters of the solution

  C = concentration of the solution in moles per liter

  T = temperature in K

  R or S = 0.08211 atm deg$^{-1}$ mole$^{-1}$

- $\pi V = \dfrac{w}{M_0} ST \quad \left( \because n = \dfrac{w}{M_0} \right); M_0 = \dfrac{wST}{\pi V}$ ($M_0$ = molecular weight of solute)

  where $\quad$ w = Wt. of solute in g dissolved in $V_1$ of solution.

  m = molecular wt. of the solute; $\pi$ = hdg

- In isotonic solutions, since osmotic pressure p is equal, their concentration (C) must also be equal,

  i.e., $\dfrac{n_1}{V_1} = \dfrac{n_2}{V_2}; \quad \dfrac{w_1}{m_1 V_1} = \dfrac{w_2}{m_2 V_2}$

- If a number of solutes is present in the solutions and $\pi_1, \pi_2, \pi_3,$ etc. are their individual osmotic pressure, then the total osmotic pressure = $\pi_1 + \pi_2 + \pi_3 + \ldots$

**T P Varun (JEE 2012, AIR 64)**

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## 6.4.2 Reverse Osmosis

Generally, we understand that if a pressure higher than osmotic pressure is applied on a solution, then the solvent will flow from the solution into the pure solvent through the semipermeable membrane. However, here as the flow of solvent is in the reverse direction to that observed in the usual osmosis, we call this process as reverse osmosis. This process is extensively used in the desalination of sea water to obtain pure water.

## 6.4.3 Isotonic Solutions

A pair of solutions having the same osmotic pressure are known as isosmotic or isotonic solutions. However, if two such solutions are separated by a semipermeable membrane, then there will be transference of solvent from one solution to the other. Thus, isosmotic solutions that are separated using a semipermeable membrane are known as isotonic solutions. Further, isotonic solutios have the same concentration.

For example, 0.85% NaCl solution is found to be isotonic with blood, while 0.9% NaCl solution isotonic with human RBCs. On the contrary, a solution that is having lower or higher osmotic pressure than the other is said to be hypotonic or hypertonic, respectively with respect to other solution. (i) When placed in water or hypotonic solutions, cells swell and burst and this process is known as hemolysis. (ii) When placed in hypertonic solutions, the fluid from the plant cells comes out and thus the cells contract in size. This process is known as plasmolysis. Further, when excess of fertilizers (like urea) is applied, then plasmolysis takes place and hence plants dry up (wilt).

**Illustration 7:** Estimate the boiling point of a solution of 25.0 g of urea ($NH_2CONH_2$) plus 25.0 g of thiourea ($NH_2CSNH_2$) in 500 g of chloroform, $CHCl_3$. The boiling point of pure chloroform is 61.2°C, $K_b$ of chloroform = 3.63 $km^{-1}$. **(JEE MAIN)**

**Sol:** Molality is given by moles of Solute by mass of solvent in Kg. since here two solute are used we have to first calculate the mole of urea and thiourea used. The sum of the two solute will give us total moles of solute which can be used to calculat the molality of the solution.

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

$$\text{Moles of thiourea} = \frac{25.0g}{76g/mol} = 0.33 mol$$

$\therefore$ Total moles of solute = 0.42 + 0.33 = 0.75

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

$\Delta T_b = T_b - T_b° = K_b.m = 3.63 \times 1.50 = 5.44$ K = 5.445°C

$T_b = 5.445°C + T_b° = 5.445°C + 61.2°C = 66.645°C$

**Illustration 8:** Consider a vertical tube of cross-section area of 1 $cm^2$. The bottom of the tube is closed with a semipermeable membrane and 1 g of glucose is placed in the tube. The closed end of the tube is immersed in pure water. What will be the height of the liquid level in the tube at equilibrium? The density of solution may be taken as 1 $g/cm^2$. What is the osmotic pressure at equilibrium at 25°C? Assume negligible depth of immersion of tube. **(JEE ADVANCED)**

**Sol:** Since here we have to calculate the osmotic pressure, we can use the following relation $\pi V = nRT$

Volume term is not provided instead cross section area of the tube is given so from this we can calculate the volume term.

Let height of the tube = h cm

$V = (h \times 1)$ $cm^3$ $\qquad \because$ cross-sectional area = 1 $cm^2$

$\pi V = nRT; \pi \times \left(\dfrac{h \times 1}{1000}\right) = \dfrac{1}{180} \times 0.0821 \times 298; \pi = \dfrac{134.92}{h}$ atm

$\pi = h \times d \times g; \dfrac{134.92}{h} = \dfrac{h \times 1}{100} \times \dfrac{9.8}{101.325},$ 1 atm = 101.325 $KP_a$

h = 375 cm = 3.75 m

$\pi = h \times d \times g = 3.75 \times 1 \times 9.8 = 36.7$ $KP_a$

**Illustration 9:** A solution containing 0.2563 g of nephthalene (molecular mass = 128) in 50 g of carbon tetrachloride yields a boiling point elevation of 0.201°C while a solution of 0.6216 g of an unknown solute in the same mass of the solvent gives a boiling point elevation of 0.647°C. Find the molecular mass of the unknown solute. **(JEE MAIN)**

**Sol:** From the given dataa first calculate $K_b$ by using following formula $K_b = \dfrac{\Delta T_b \times W \times m}{1000 \times w}$;

Now by using the value of Kb find out the molecular mass of the unknown solute.

We know that,

$K_b = \dfrac{\Delta T_b \times W \times m}{1000 \times w}$; for $CCl_4$, $K_b = \dfrac{0.201 \times 50 \times 128}{1000 \times 0.2563} = 5.019$

$K_b$ is now used in the second part of the problem; $m = \dfrac{1000 \times 5.019 \times 0.6216}{0.647 \times 50} = 96.44$
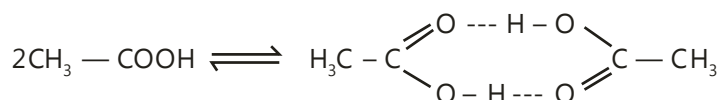
**Illustration 10:** In a cold climate, water is frozen causing damage to radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at –6°C ($K_f$ for water = 1.85 K kg mol$^{-1}$). **(JEE ADVANCED)**

**Sol:** Here we are provided with the value of $\Delta T$ ,W ,m and $K_f$ so we can calculate th weight by using the following formual:

$w = \dfrac{m \times M \times \Delta T_f}{1000 \times K_f}$ Given, $\Delta T$ = 6°C, W = 4kg = 4000g, m = 62, $K_f$ = 1.85; $w = \dfrac{m \times M \times \Delta T}{1000 \times K_f} = \dfrac{62 \times 4000 \times 6}{1000 \times 1.85} = 804.32$ g

## 6.5 Abnormal Molar Masses

**Association :** Association of molecules generally leads to decrease in the number of particles in a solution and this results in a decrease in the value of colligative property. As we are aware, colligative property is inversely related to the molecular mass. Therefore, obviously a higher value is obtained for molecular mass. For example, when ethanoic acid is dissolved in benzene, it undergoes dimerization and shows a molecular mass of 120 (normal molecular mass is 60).



$$2CH_3 - COOH \rightleftharpoons \quad H_3C - C \begin{matrix} O \text{ --- } H - O \\ \diagup \qquad\qquad \diagdown \\ O - H \text{ --- } O \end{matrix} C - CH_3$$

**Dissociation :** In contrast to association, dissociation leads to an increase in the number of solute particles in a solution and this results in an increase in the value of colligative property. Further, since colligative property is inversely related to the molecular mass molecular mass of such a substance as calculated from colligative property will therefore be less than its normal value. For example, we know that KCl is an electrolyte. However, when it is dissolved in water it dissociates into $K^+$ and $Cl^-$ ions and there would be double the number of particles if there is complete dissociation. Hence, it is expected to have molecular mass 37.25 g = 74.5/2. $KCl \rightleftharpoons K^+ + Cl^-$

To account for the above anomalies, van't Hoff therefore introduced a factor 'i' in the van't Hoff equation ($\pi V = RT$) of osmotic pressure. Accordingly, the modified equation may thus be written as $\pi V = iRT$. The factor 'i' is defined

by the expression, $\quad i = \dfrac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}}$

In this regard, the experimental value of i can be obtained by dividing the observed osmotic pressure of the solution under the study with that of the solution of a normal substance (say, e.g., sucrose) of the same concentration (molarity) as that of the substance under study.

Now, since osmotic pressure behaves like other colligative properties, the factor i can also be applied to other colligative properties. Thus, in general,

$i = \dfrac{\text{Actual number of particles}}{\text{No. of particle when no ionisation/association}}$ ; $i = \dfrac{\text{Observed colligative property (experimental)}}{\text{Normal colligative property(calculated)}}$

Now, since molecular weight of a solute is inversely proportional to the colligative property the factor 'i' may also be defined in the following way.

$i = \dfrac{\text{Normal molecular wt. (calculated value)}}{\text{Observed molecular wt.(experimental value)}}$

Evidently, for a normal substance (which neither dissociates nor associates in solution), the factor 'i' is always unity.

When the van't Hoff factor is included, then the colligative properties get modified shown hereunder.

(a) Relative Lowering in Vapor pressure

$$\frac{P^0 - P_s}{P^0} = i \times X_B \text{ where} \quad i = \text{van't Hoff factor}$$

$X_B$ = mole fraction of solute for dilute solution $\frac{P^0 - P_s}{P^0} = i \times \frac{n_B}{n_A}$ ; $n_B$ = number of moles of solute; $n_A$ = number of moles of solvent

$$\Rightarrow \frac{P^0 - P_s}{P^0} = i \times \frac{W_B}{M_B} \times \frac{M_A}{W_A} \text{ where } W_B = \text{amount of solute dissolved; } W_A = \text{amount of solvent taken;}$$

$M_B$ = molecular mass of solute; $M_A$ = molecular mass of solvent

Elevation in Boiling point

$$\Delta T_B = iK_b m ; \quad \Delta T_B = iK_b \times \frac{W_B}{M_B \times W_A (gms)} \times 1000$$

Depression in Freezing Point

$$\Delta T_f = iK_f m ; \quad \Delta T_f = iK_f \times \frac{W_B}{M_B \times W_A (gms)} \times 1000$$

Osmotic pressure

$\pi V = inRT; \pi = iCRT$

## 6.6 Relationship Between van't Hoff Factor for Dissociation and Association

### (a) Dissociation

**Degree of dissociation:** We define the degree of dissociation as the number of moles dissociated over the initial concentration taken

Van't Hoff factor : $\dfrac{\text{Total number of particles at equilibrium}}{\text{Initial concentration}}$

Let c moles per liter of an electrolyte $A_x b_y$ be taken and let it dissociate

as $xA^{y+}$ & $yB^{x-}$. '$\alpha$' be degree of dissociation.

∴ No. of solute particle dissociated = C$\alpha$

$$A_x B_y \rightarrow xA^{y+} + yB^{x-}$$

Initial conc.         C        O      O

Conc. at equilibrium  C − C $\alpha$     x c $\alpha$    y c $\alpha$

$i = \dfrac{[(c - c\alpha) + xc\alpha + Yc\alpha]}{c}$      $\Rightarrow$    $i = \dfrac{1 - \alpha + x\alpha + y\alpha}{1} = 1 + [(x + y) - 1] a$

Let x + y = n = number of particles formed after dissociation

$$\Rightarrow \quad i = 1 (n - 1) \alpha; \alpha = \frac{i - 1}{n - 1}$$

### (b) Association

**Degree of Association:** The degree of association may be defined as the number of molecules associated over initial concentration.

$\alpha = \dfrac{\text{number of moles associated}}{\text{Initial concentration}}$ ; $i = \dfrac{\text{Total number of moles of particles at equilibrium}}{\text{Initial concentration}}$

Let n molecules of an electrolyte A undergo association

     $nA \rightarrow A_n$
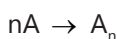
Let the initial concentration of A = C; the degree of association = a

when $C\alpha$ moles of A associate, then $\dfrac{C\alpha}{n}$ moles of $A_n$ are formed

Number of moles of equilibrium $(C - C\alpha)\dfrac{C\alpha}{n}$ $\Rightarrow$ $\quad$ i = $\dfrac{C - C\alpha + \dfrac{C\alpha}{n}}{C}$

If C = 1, then i = $\dfrac{1 - \alpha + \dfrac{\alpha}{n}}{1}$ ; i = 1 + $\left(\dfrac{1}{n} - 1\right)\alpha$ $\Rightarrow$ $\quad$ $\alpha = \dfrac{i - 1}{\dfrac{1}{n} - 1}$

**Illustration 11:** The freezing point depression of 0.001m $K_x[Fe(CN)_6]$ is $7.10 \times 10^{-3}$ K. Determine the value of x. Given, $K_f$ = 1.86 K kg mol$^{-1}$ for water. **(JEE MAIN)**

**Sol:** $\Delta x = i \times K_f \times m$; $7.10 \times 10^{-3} = i \times 1.86 \times 0.001$; i = 3.817

$\alpha = \dfrac{i - 1}{n - 1}$; $1 = \dfrac{3.817 - 1}{(x + 1) - 1}$; x = 2.817 $\approx 3$

∴ Molecular formula of the compound is $K_3[Fe(CN)_6]$.

**Illustration 12:** Three particles of a solute, A, associate in benzene to form species $A_3$. Calculate the freezing point of 0.25 molal solution. The degree of association of solute A is found to be 0.80, the freezing point of benzene and its cryoscopic constant are 5.5°C and 5.12 km$^{-1}$, respectively. **(JEE MAIN)**

**Sol:** $\qquad\qquad\qquad\qquad$ 3A $\quad\rightarrow\quad$ $A_3$

No. of moles dissolved $\qquad$ 3m(1 − $\alpha$) $\qquad$ 0

No. of moles after dissociation m$\alpha$/3

Total moles present after dissociation

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

$\Delta T_f = K_f m$ or $\quad T_f^0 - T_f = 5.12$ km$^{-1}$ × 0.117 m = 0.6

$T_f = T_f^0 - 0.6°C = 5.5°C - 0.6°C = 4.9°C$

# PROBLEM-SOLVING TACTICS

General Plan for Solving Problems Involving Freezing Point Depression and Boiling Point Elevation
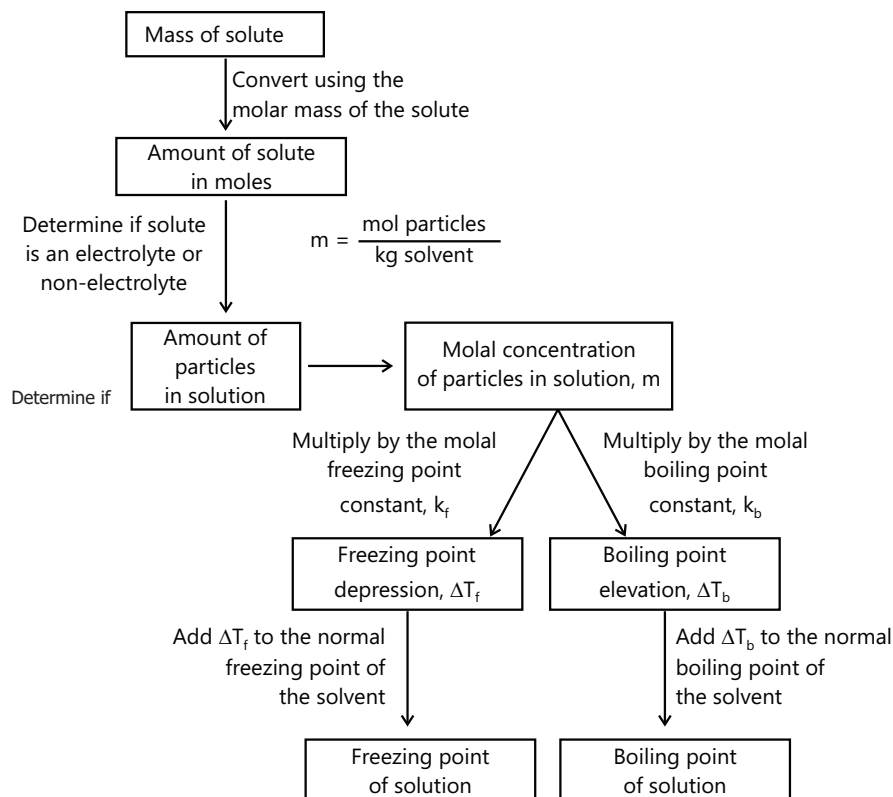


**Figure 20.7**

For example, let us consider the table provided hereunder.

**Table:** List of freezing point depression and boiling point elevation constant for common solvents.

| Solvent | Normal f.p. (in °C) | $k_f$ (in °C/m) | Normal b.p. (in °C) | $k_b$ (in °C/m) |
|---|---|---|---|---|
| Acetic acid | 16.6 | −3.90 | 117.9 | 3.07 |
| Camphor | 178.8 | −39.7 | 207.4 | 5.61 |
| Ether | −116.3 | −1.79 | 34.6 | 2.02 |
| Naphthalene | 80.2 | −6.94 | 217.7 | 5.80 |
| Phenol | 40.9 | −7.40 | 181.8 | 3.60 |
| Water | 0.00 | −1.86 | 100.0 | 0.51 |

**Sample Problem 1:** What is the freezing point of a solution of 210.0 g of glycerol, $HOCH_2CHOHCH_2OH$, dissolved in 350 g of water?

**Sol 1: Analyze**

| (i) What is given in the problem? | The formula and mass of solute and the mass of the water used |
|---|---|
| (ii) What are you asked to find? | The freezing point of the solution |

| Items | Data |
|---|---|
| Identity of solute | Glycerol, $HOCH_2CHOHCH_2OH$ |
| Particles per mole of solute | 1 mol |
| Identity of solvent | Water |
| Freezing point of solvent | 0.00°C |
| Mass of solvent | 350 g |
| Mass of solute | 210.0 g |
| Molar mass of solute | 92.11 g/mol |
| Molal concentration of solute particles | ? |
| Molal freezing point constant for water | −1.86° C/m |
| Freezing point depression | ? |
| Freezing point of solution | ? |

## 2. Plan

What steps are needed to calculate the freezing point of the solution?

In such cases, use the molar mass of the solute to determine the amount of solute. Then, apply the mass of solvent to calculate the molality of the solution.

From the molality, now use the molal freeezing constant for water to calculate the number of degrees the freezing point is lowered. Thereafter, add this negative value ot the normal freezing point.

Mass of glycerol in g
|
Multiply by the inverse
of the molar mass
of glycerol
↓
2
Amount of glycerol in solution
|
The solute is a non electrolyte,
so the amount of solute
equals the amount
of particles in solution
↓
3
Amount of particles in solution → Divide the amount of the particles in Solution by the mass of the solvent in kilograms →

Freezing point of the glycerol solution
6
↑
Add $T_f$ to the
normal freezing point
of water
|
5
Freezing point elevation, $\Delta T_f$
↑
Multiply by the molal
freezing point constant
$K_f$ of water
|
4
Molal concentration of
particles in water, m
↑
Mass of water in kg
↑
Multiply by the conversion factor $\dfrac{1 \text{ kg}}{1000 \text{ g}}$
|
Mass of water in g

$$\overset{\text{given}}{gH_2O} \times \frac{1 \text{ kg}}{1000 \text{ g}} = kg \, H_2O$$

$$\overset{\text{given}}{g \text{ glycerol}} \times \underset{\substack{\text{molar mass of glycerol}}}{\overset{\frac{1}{}}{\frac{1 \text{ mol glycerol}}{92.11 \text{ g glycerol}}}} \times \overset{\substack{\text{Calculate} \\ \text{above}}}{\frac{1}{kg \, H_2O}} \times \overset{\substack{\text{freezing point} \\ \text{depression} \\ \text{constant}}}{\frac{-1.86° C}{mol / kg}} = \Delta T_f; \quad \overset{\substack{\text{freezing point} \\ \text{of } H_2O}}{0.00° C} \quad + \quad \overset{\substack{\text{Calculated} \\ \text{above}}}{\Delta T_f} = t_f$$

### 3. Compute

$$350 \text{ g H}_2\text{O} \times \frac{1\text{kg}}{1000\text{g}} = 0.350 \text{ kg H}_2\text{O}$$

$$210.0 \text{ g glycerol} \times \frac{1 \text{ mol glycerol}}{92.11 \text{ g glycerol}} \times \frac{1}{0.350\text{kg H}_2\text{O}} \times \frac{-1.86^\circ\text{C}}{\text{mol} / \text{kg}} = -12.1^\circ\text{C}$$

$$0.00^\circ\text{C} + (-12.1^\circ\text{C}) = -12.1^\circ\text{C}$$

### 4. Evaluate

| | |
|---|---|
| (i) Are the units correct? | Yes, units canceled to give Celsius degrees. |
| (ii) Is the number of significant figure correct? | Yes, three significant figures are correct because the data had a minimum of three significant figures. |
| (iii) Is the answer reasonable? | Yes, the calculation can be approximated as |

$$200 \div [90 \times 3(350 \div 1000)] \times -2 = -400/30 = -13, \text{ which is close to the calculated value.}$$

**Sample Problem 2:** What is the boiling point of a solution containing 34.3 g of the ionic compound magnesium nitrate dissolved in 0.107 kg of water?

**Sol:**

### 1. Analyze

| (i) What is given in the problem? | the formula and mass of solute and the mass of the water used |
|---|---|
| (ii) What are you asked to find? | the freezing point of the solution |

| Items | Data |
|---|---|
| Identity of solute | Magnesium nitrate |
| Equation for the dissociation of the solute | $Mg(NO_3)_2 \rightarrow Mg^{2+} + 2NO_3^-$ |
| Amount of ions per mole of solute | 3 mol |
| Identity of solvent | Water |
| Boiling point of solvent | 100.0°C |
| Mass of solvent | 0.107 kg $H_2O$ |
| Mass of solute | 34.3 g |
| Molar mass of solute | 148.32 g/mol |
| Molal concentration of solute particles | ?m |
| Molal boiling point constant for solvent | 0.51°C/m |
| Boiling point depression | ?°C |
| Boiling point of solution | ?°C |

### 2. Plan

What steps are needed to calculate the freezing point of the solution?

In such a case, use the molar mass to calculate the amount of solute in moles. Then, multiply the amount of solute by the number of moles of ions produced per mole of solute. Use the amount of ions with the mass of solvent to compute the molality of particles in solution. Thereafter, use this effective molality to determine the boiling point elevation and the boiling point of the solution.
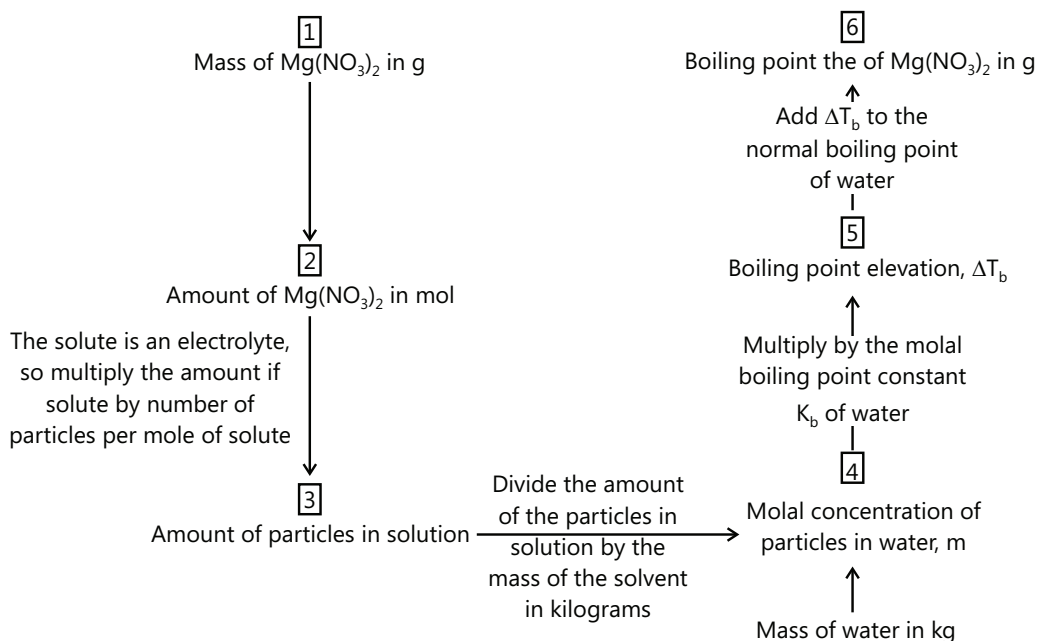
$$\underset{\text{given}}{\text{g Mg(NO}_3)_2} \times \frac{1 \text{ mol Mg(NO}_3)_2}{148.32 \text{ g Mg(NO}_3)_2} \times \frac{3 \text{ mol particles}}{1 \text{ mol Mg(NO}_3)_2} \times \underset{\text{given}}{\frac{1}{\text{kg H}_2\text{O}}} \times \underset{\substack{\text{molal boiling-point} \\ \text{constant for water}}}{\frac{0.51^\circ\text{C}}{\text{mol/kg}}} = \Delta t_b$$

$$\underset{\substack{\text{boiling point} \\ \text{of H}_2\text{O}}}{100.0^\circ\text{C}} + \underset{\substack{\text{Calculate} \\ \text{above}}}{\Delta t_b} = t_b$$

### 3. Compute

$$34.3\text{g Mg(NO}_3)_2 \times \frac{1 \text{ mol Mg(NO}_3)_2}{148.32 \text{ g Mg(NO}_3)_2} \times \frac{3 \text{ mol particles}}{1 \text{ mol Mg(NO}_3)_2} \times \frac{1}{0.107 \text{kg H}_2\text{O}} \times \frac{0.51^\circ\text{C}}{\text{mol/kg}} = 3.31^\circ\text{C}$$

100. 0°C + 3.31°C) = 103.3°C

### 4. Evaluate

| | |
|---|---|
| (i) Are the units correct? | Yes, units canceled to give Celsius degrees. |
| (ii) Is the number of significant figure correct? | Yes, the number significant figures is correct because the boiling point of water was given to one decimal place. |
| (iii) Is the answer reasonable? | Yes, the calculation can be approximated as [35 × 3)/150 × 5 = (7/10) × 5 = 3.5, which is given to one decimal place. |

# POINTS TO REMEMBER

| | |
|---|---|
| Henry's law | $P = K_H X$, where, $P$ = partial pressure of a gas over solution, $K_H$ = Henry's constant, $X$ = mole fraction of the gas in solution |
| Raoult's law | $P = X_A P_A^0 + X_B P_B^0$, where, $P$ = total pressure of the solution, $X_A$ and $X_B$ = mole fraction of substituents A and B. $p_A{}^\circ$ and $P_B^0$ = partial pressure of A and B, respectively |
| Relationship between Dalton's law and Raoult's law | $Y_A = \dfrac{X_A P_A^0}{P} = \dfrac{P_A}{P}$, $Y_B = \dfrac{X_B P_B^0}{P} = \dfrac{P_B}{P}$, where, $Y_A$ and $Y_B$ denotes mole fraction of components A and B in vapor phase |
| Lowering of vapor pressure | $\dfrac{P_A^0 - P}{P_A^0} = x_B$, relative lowering of vapor pressure = mole fraction of solute |
| Elevation in boiling point | $\Delta T_B = \dfrac{K_B W_B}{M_B \times W_A} \times 1000$ |
| Depression in freezing point | $\Delta T_f = \dfrac{RT_f \times w_{solute}}{M_{solute} \times W_{solvent}} \times 1000$ |
| Osmotic pressure | Osmotic pressure, $\pi = CRT$ |
| van't Hoff factor, i | $i = \dfrac{\text{Normal molecular wt.(calculated value)}}{\text{Observed molecular wt.(experimental value)}}$ |
| van't Hoff factor in case of association | For association, $\alpha = \dfrac{i-1}{n-1}$ |
| van't Hoff factor in case of dissociation | For dissociation, $\alpha = \dfrac{i-1}{\dfrac{1}{n}-1}$ |

## Solved Examples

### JEE Main/Boards

**Example 1:** One litre of sea water weighs 1030 g and contain about $6 \times 10^{-3}$ g of dissolved $O_2$. Calculate the concentration of dissolved oxygen in ppm.

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

ppm of $O_2$ in 1030 g sea water

$= \dfrac{\text{Mass of } O_2 \text{ in mg}}{\text{Mass of sea water in mg}} \times 10^6$

$= \dfrac{6}{(1030 \times 1000)\text{mg}} \times 10^6$ = 5.8 ppm

**Example 2:** The osmotic pressure of a solution of an organic substance containing 18 g in one litre of solution at 293 K is $2.414 \times 10^5$ Nm$^{-2}$. Find the molecular mass of the substance if S = 8.3 JK$^{-1}$ per mol.

**Sol:** Applying the equation, $PV = \dfrac{w}{m} \cdot ST$ or $m = \dfrac{w}{PV} \cdot ST$

Given, P = $2.414 \times 10^5$ Nm$^{-2}$,

V = 1.0 liter = $1 \times 10^{-3}$ m$^3$,

S = 8.3 JK$^{-1}$ per mol,

w = 18 g and T = 293 K

$m = \dfrac{18}{2.414 \times 10^5 \times 1 \times 10^{-3}} \times 8.3 \times 293 = 181.33$

**Example 3:** What is the molality of 40.0 wt% ethylene glycol solution used for automobile antifreeze ? (molar mass of ethylene glycol = 62 g mol⁻¹).

**Sol:** 100 g ethylene glycol solution has

= 40 g ethylene glycol

60 g water (solvent) has = 40 g ethylene glycol

Or 0.060 kg water has

$= \dfrac{40}{62}$ mole ethylene glycol

∴ Molality = $\dfrac{\text{mole of solute}}{\text{kg of solvent}} = \dfrac{40/62}{0.060} = 10.75$ molal

**Example 4:** To 500 cm³ of water 3.0 × 10³ kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point ? $K_f$ and density of water are 1.86 K kg⁻¹ and 0.997 g cm⁻³, respectively.

**Sol:** Mass of solute = 3 × 10⁻³ kg = 3 g

Mass of solvent = 500 × 0.997 = 498.5 g

α = 23% = 0.23,

i = 1 − α + nα = 1 − 0.23 + 2 × 0.23 = 1.23

$\Delta T_f = i(\text{molality} \times K_f)$

$\Rightarrow 1.23 \times \left(\dfrac{3 \times 1000}{60 \times 498.5}\right) \times 1.86 \Rightarrow \Delta T_f = 0.229$

**Example 5:** Concentration of NaOH solution is 3.0 molal and its denisty is 1.110 g/mL. What is the molarity of the solution?

**Sol:** Molarity = $\dfrac{w}{M} \times \dfrac{1000}{V}$

[V = volume of the solution]

3 mol. of NaOH = 120 g of NaOH

Weight of the solution = [120 + 1000] g

$= 1120$ g

1.110 g solution has the volume = 1 c.c.

∴ 1120 g solution has the volume = $\dfrac{1}{1.110} \times 1120$

Hence, molarity = $\left[\dfrac{w}{M}\right] \times \dfrac{1000}{V}$

$= 3 \times \dfrac{1000}{1120} \times 1.110 = 2.9732M$

**Example 6:** Why does the use of the pressure cooker reduces cooking time?

**Sol:** At higher pressure over the liquid (due to weight of the pressure cooker lid) the liquid boils at higher temperaure and cooking occurs faster.

**Example 7:** One liter of a sample of hard water contains 1 mg of $CaCl_2$ and 1 mg of $MgCl_2$. Find the total hardness in terms of parts of $CaCO_3$ per 10⁶ parts of water by mass.

**Sol:** $CaCl_2 \rightarrow CaCO_3$

111 g    100 g

∴ 1 mg of $CaCl_2$ is equivalent to $\left(\dfrac{100}{111} \times 1\right)$ mg $CaCO_3$

$MgCl_2 \rightarrow CaCO_3$

95        100

∴ 1 mg of $MgCl_2$ is equivalent to $= \left(2 \times \dfrac{1}{3}\right) = 0.82$ mg

Total mass of $CaCO_3 = \left(\dfrac{100}{111} + \dfrac{100}{95}\right)$ mg

= 1.9535 mg

Given volume = 1 liter, mass

= 1000 g = 10⁶ mg

Thus, 1.9535 mg of $CaCO_3$ is present in 10⁶ mg of $H_2O$.

Hardness = 1.9535 ppm

**Example 8:** Vapor pressure of mixtures of $C_6H_6$ and $C_7H_8$ at 50°C are given by $P_M = 179 X_B + 92$, respectively where $X_B$ is the mole fraction of $C_6H_6$. Calculate

(a) Vapor pressure of pure liquids.

(b) Vapor pressure of liquid mixture obtained by mixing 936g $C_6H_6$ and 736 g toluene.

(c) If the vapors are removed and condensed into liquid and again brought to the temperture of 50°C, what would be the mole fraction of $C_6H_6$ in vapor state?

**Sol:** Given, $P_M = 179X_B + 92$

For pure $C_6H_6$,

$X_B$, i.e., mole fraction of benzene = 1

∴ $P_B^0 = 179 + 92 = 271$ mm

(a) For pure $C_7H_8$; XB = 0

∴ $P_T^0 = 179 \times 0 + 92 = 92$ mm

(b) $X_B = \dfrac{\dfrac{936}{78}}{\dfrac{936}{78}+\dfrac{736}{92}} = \dfrac{12}{12+8} = 0.60$

$X_T = \dfrac{\dfrac{736}{92}}{\dfrac{936}{78}+\dfrac{736}{92}} = \dfrac{8}{12+8} = 0.40$

$P_M = 179 \times 0.6 + 92 = 107.4 + 92 = 199.4$ mm

(c) Mole fraction of $C_6H_6$ in vapor phase of initial mixture $X'_B = P'_B / P_M$

$\therefore X'_B = [271 \times 0.6] / 199.4 = 0.815$

Similarly, $X'_T = [92 \times 0.4] / 199.4 = 0.185$

These fractions of vapors are taken out and condensed into liquid. The liquid is again brought to 50°C to get again vapour–liquid equilibrium.

$\therefore$ Mole fraction of components in vapor phase of initial mixture = Mole fraction of components in liquid phase of II mixture.

$\therefore P_M = P_B^0 \cdot X'_B + P_T^0 \cdot X'_T$

$= 271 \times 0.815 + 92 \times 0.185$ mm

$= 220.865 + 17.02 = 237.885$ mm

**Example 9:** The solution of a non-volatile solute in water freezes at –0.30°C. The vapor pressure of pure water at 298 K is 23.51 mm $H_g$ and $K_f$ of water is 1.86 degree/molal. Calculate the vapor pressure of this solution at 298 K.

**Sol:** $\Delta T_f$ = molality $\times K_f$; 0.30 = molality $\times$ 1.86

molality $= \dfrac{0.30}{1.86} = \dfrac{10}{62} = \dfrac{5}{31} \Rightarrow \dfrac{n \times 1000}{W(gm)}$

n = moles of solute, W = wt. of solvent

M = mol. wt. solvent, N = mole of solvent

$\dfrac{n}{N \times 18} = \dfrac{5}{31 \times 1000}$

$\Rightarrow \dfrac{n}{N} = \dfrac{5 \times 18}{31 \times 1000} = \dfrac{9}{3100}$

$\therefore P_S = \dfrac{N}{n+N} P^0 \qquad \Rightarrow \quad \dfrac{\dfrac{N}{n}}{1+\dfrac{N}{n}} P_0$

$\Rightarrow P_S = \dfrac{\dfrac{3100}{9}}{1+\dfrac{3100}{9}} \times 23.51 = 23.442$ mm

**Example 10:** x g of non-electrolytic compound (molar mass = 200) is dissolved in 1.0 liter of 0.05 M NaCl solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C. Calculate the value of 'x.' Assume complete dissociation of NaCl and ideal behavior of this solution.

**Sol:** (i) For NaCl; $\pi_1 = i(CRT)$

$\pi_1 = 2 \times 0.05 \times 0.0821 \times 300 ; \Rightarrow \pi_1 = 2.463$ atm

For unknown compound

$\pi_2 = CRT \Rightarrow \pi_2 = \dfrac{x}{200 \times 1} \times 0.821 \times 300 ;$

$\Rightarrow \pi_2 = 0.1231 \times$ atm

Total osmotic pressure $\pi = \pi_1 + \pi_2$

$4.92 = 2.463 + 0.1231x; \quad x = 19.959$ g

## JEE Advanced/Boards

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

**Sol:** Let the VP of pure A and B are $P_A^0$ and $P_B^0$, respectively.

Total VP of solution (1 mole A + 3 moles B)

$P_M = X_A P_A^0 + X_B P_B^0 \Rightarrow 550 = \dfrac{1}{4} P_A^0 + \dfrac{3}{4} P_B^0$

or $\quad P_A^0 + 3P_B^0 = 2200$ ... (i)

Total VP of solution (1 mole A + 4 moles B)

$P_M = \dfrac{1}{5} P_A^0 + \dfrac{4}{5} \dfrac{1}{5} P_B^0 \Rightarrow 560 = \dfrac{1}{5} P_A^0 + \dfrac{4}{5} P_B^0$

or $\quad P_A^0 + 4P_B^0 = 2800$ ... (ii)

Solving (i) and (ii)

$P_A^0 = 400$ mm of Hg $\qquad P_B^0 = 600$ mm of Hg

**Example 2:** Two liquids A and B form an ideal solution at temperature T. When the total vapor pressure above the solution is 400 torr, the mole fraction of A in the vapor phase is 0.40 and in the liquid phase 0.75. What are the vapor pressure of pure A and pure B at temperature T?

**Sol:** Mole fraction of A in vapor phase $Y_A = 0.4$ and in liquid phase $X_A = 0.75$

$P_{Total}$ = 400 torr

Let VP of pure A and B are $P_A^0$ and $P_B^0$

$X_A P_A^0 = Y_A P_{Total}$

$P_A^0 = \dfrac{Y_A P_{Total}}{X_A} = \dfrac{0.4 \times 400}{0.75} = \dfrac{160}{0.75}$

$P_A^0$ = 213.33 torr.

$P_{Total} = X_A P_A^0 + (1 - X_A)P_B^0$

$400 = 0.75 \left( \dfrac{160}{0.75} \right) P_B^0 + (1 - 0.75),$

$P_B^0$ = 960 torr

**Example 3:** Calculate the freezing point of an aqueous solution of nonelectrolyte having an osmotic pressure of 0.2 atmosphere at 300 K.

($K_f$ = 1.86 K kg mol$^{-1}$, R = 0.821 liter-atm K$^{-1}$ mol$^{-1}$) (assume molarity = molality)

**Sol:** $\pi$ = CRT, C = $\dfrac{\pi}{RT} = \dfrac{2}{0.0821 \times 300}$ mol lit$^{-1}$

In dilute solution, the density of water can be taken as 1.90 gm cm$^{-3}$.

Hence, molality $\approx$ molarity

$\Delta T_f = (\text{molalty} \times K_f) = \dfrac{2}{0.0821 \times 300} \times 1.86 ; \Rightarrow \Delta T_f = 0.151$ K

$\because (T_f)_{solution} = (T_f)$ solvent $- \Delta T_f$ = (273 - 0.151)

$(T_f)_{solution}$ = 272.749 K or $-0.151$°C

**Example 4:** Vapor pressure of water at 293 K is 17.51 mm. Lowering of vapor pressure of a sugar solution is 0.0614 mm. Calculate (i) relative lowering of vapor pressure, (ii) vapor pressure of the solution and (iii) mole fraction of water.

**Sol:** Here, we are given that

vapor pressure of water; ($P^0$) = 17.51 mm

Lowering of vapor pressure

($P^0 - P_s$) = 0.0614 mm

(i) Relative lowering of vapor pressure

$= \dfrac{P^0 - P_s}{P^0} = \dfrac{0.0614\text{mm}}{17.51\text{mm}} = 0.00351$

(ii) Vapor pressure of the solution ($P_s$)

$P^0 - P_s$ = 0.0614 mm; $P^0$ = 17.51 mm

$\therefore$ 17.51mm $- P_s$ = 0.0614 mm

or $P_s$ = 17.51 mm $-$ 0.0614 mm = 17.4468 mm

(iii) To calculate mole fraction of water

By Raoult's law, $\dfrac{P^0 - P_s}{P^0} = \dfrac{n_B}{n_A + n_B} = X_B$ ,

mole fraction of solute, i.e.,

$X_B = \dfrac{P^0 - P_s}{P^0} = 0.00351$

$\therefore$ Mole fraction of solvent (water),

$X_A = 1 - x_B = 1 - 0.00351 = 0.99649$

**Example 5:** Ethylene dibromide ($C_2H_4Br_2$) and 1,2-dibromo propane form a series of ideal solutions over the whole range of composition. At 85°C, the vapor pressure of these two liquids are 173 and 127 torr, respectively. What would be the mole fraction of ethylene dibromide in a solution at 85°C equilibrated with 1:1 molar mixture in the vapor?

**Sol:** Suppose the mole fraction of ethylene dibromide in the liquid phase = x. Then, mole fraction of 1,2-dibromo propane will be = 1 − x.

Vapor pressure of ethylene dibromide

$= x \times P^0 = x \times 173$ torr $= 173$ x torr

Vapor pressure of 1,2-dibromo propane

$= (1 - x) \times 127$ torr

As they have 1:1 molar ratio in the vapor phase,

173 x = (1 − x) × 127 or 173 x = 127 − 127x

or 300x = 127 or x = $\dfrac{127}{300}$ = 0.423

**Example 6:** Vapor pressure of solution containing 6 g of a non-volatile solute in 180 g water is 20.0 torr. If 1 mol water is further added vapor pressure increases by 0.02 torr. Calculate vapor pressure of water and molecular weight of non-volatile solute with temperature remaining constant.

**Sol:** Let molecular wt. of solute = m

and VP of water (solvent) = $P^0$

$P_{solution}$ = 20 torr

moles of solute, n = $\dfrac{6}{m}$

moles of solvent, N = $\dfrac{180}{18}$ = 10

$\therefore P_s = \left( \dfrac{N}{n+N} \right) P^0$

$\Rightarrow 20 = \left( \dfrac{10}{\dfrac{6}{m}+10} \right) P^0 = \left( \dfrac{10m}{6+10m} \right) P^0$ ... (i)

If 1 mol water is further added, then moles of solvent N = 10 + 1 = 11 mol and VP of solution becomes

Ps = 20 + 0.02 = 20.02 torr

$$\Rightarrow P_s = \frac{N}{n+N} P^0$$

$$20.02 = \left(\frac{11}{\frac{6}{m}+11}\right) = \left(\frac{11m}{6+11m}\right) P^0 \qquad ... (ii)$$

Now, divide (2) by (1)

$$\frac{20.02}{20} = \frac{11(6+10m)}{10(6+11m)}$$

$$\Rightarrow m = 54\ g$$

Put this value of m in (i) or (ii)

$P^0$ = 22.22 torr

**Example 7:** The density of a solution containing 13% by mass of sulfuric acid is 1.09 g/mL. Calculate the molarity and normality of the solution.

**Sol:** Volume of 100 g of the solution

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

Number of moles of $H_2SO_4$ in 100 g of the solution

$$= \frac{13}{98}$$

$$Molarity = \frac{No.\ of\ moles\ H_2SO_4}{Volume\ of\ soln.\ in\ litre}$$

$$= \frac{13}{98} \times \frac{1.09\times10}{1} = 1.445\ M$$

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

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

Similarly, normality

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

We know that,

Normality = Molarity × n

$$= 1.445 \times 2$$

$$\left[n = \frac{Mol.\ mass}{Eq.\ mass} = \frac{98}{49} = 2\right] = 2.89\ N$$

**Example 8:** Calculate the molarity, molality and mole fraction of ethyl alcohol in a solution of total volume 95 mL prepared by adding 50 mL of ethyl alcohol (density = 0.789 mL$^{-1}$) to 50 mL water (density = 1.00 g mL$^{-1}$).

**Sol:** No. of moles of ethyl alcohol

$$= \frac{Vol.\times density}{Mol.\ mass} = \frac{50\times0.789}{49} = 0.8576$$

No. of moles of water

$$= \frac{Vol.\times density}{Mol.\ mass} = \frac{50\times1}{18} = 2.7777$$

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

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

$$Molality = \frac{No.\ of\ moles\ of\ solute}{Mass\ of\ solvent\ in\ grams} \times 1000$$

$$= \frac{0.8576}{50} \times 1000 = 17.152\ m$$

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

**Example 9:** A current of dry air was bubbled through a bulb containing 26.66 g of an organic compound in 200 g of water and then through a bulb at the same temperature, containing water and finally through a tube containing anhydrous calcium chloride. The loss of mass in bulb containing water was 0.087 g and gain in mass of the calcium chloride tube was 2.036 g. Calculate the molecular mass of the organic substance.

**Sol:** $$\frac{P_0 - P_s}{P_0} = \frac{Loss\ in\ mass\ solvent\ bulb}{Gain\ in\ mass\ of\ CaCl_2\ tube} = \frac{0.087}{2.036}$$

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

$$\frac{P_0 - P_s}{P_0} = \frac{w/m}{\frac{w}{m}+\frac{W}{M}}$$

$$\frac{0.087}{2.036} = \frac{\frac{26.66}{m}}{\frac{26.66}{m}+\frac{200}{18}} = \frac{26.66}{26.66+\frac{200}{18}m}; \ m = 53.75$$

**Example 10:** 2.0 g of benzoic acid dissolved in 25.0 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant ($K_f$) of benzene is 4.9 K kg mol$^{-1}$. What is the percentage association of the acid if it forms dimer in the solution?

**Sol:** Mass of solute (benzoic acid), $w_2$ = 2.0 g

Mass of solvent (benzene), $w_1$ = 25.0 g

Observed $\Delta T_f$ = 1.62 K

$K_f$ = 4.9 K kg mol$^{-1}$

$\therefore$ Observed molar mass of benzoic acid

$M_2 = \dfrac{1000 \times K_f \times w_2}{\Delta T_f \times w_1}$

$= \dfrac{1000 \text{g kg}^{-1} \times 4.9 \text{ K kg mol}^{-1} \times 2.0 \text{g}}{1.62 \text{K} \times 25.0 \text{g}}$ = 242 g mol$^{-1}$
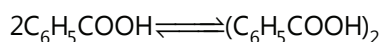
Calculated molar mass of benzoic acid

$(C_6H_5COOH)$ = 72 + 5 + 12 + 32 + 1 = 122 g mol$^{-1}$

van't Hoff factor, $i = \dfrac{\text{Calculated mol. mass}}{\text{Observed mol. mass}}$

$= \dfrac{122}{242} = 0.504$

If $\alpha$ is the degree of association of benzoic acid, then we have

$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$

| | | |
|---|---|---|
| Initial moles | 1 | 0 |
| After association | 1 – a | α/2 |

$\therefore$ The total number of moles after association

$= 1 - \alpha + \dfrac{\alpha}{2} = 0.504$

$\alpha$ = (1 – 0.504) × 2 = 0.496 × 2 = 0.992

Or percentage association = 99.2%

# JEE Main/Boards

## Exercise 1

**Q.1** How many grams of $H_2SO_4$ are required to prepare 250 mL of 0.2 molar solution?

**Q.2** A solution contains 23g of ethanol and 72g of water. Calculate the mole fraction of ethanol and water.

**Q.3** 2.82 g glucose (mo. mass = 180) are dissolved in 30g of $H_2O$. Calculate the (i) Molality of the solution (ii) Mole fraction of glucose and water.

**Q.4** Prove that the relative lowering of vapour pressure is equal to the mole fraction of non–volatile solute in the solution.

**Q.5** What is the relation between elevation of boiling point and osmosis pressure?

**Q.6** One litre aqueous solution of sucrose (molar mass = 342 g mol$^{-1}$) weighing 1015 g is found to record an osmotic pressure of 4.85 atm at 293 K. What is the molality of the sucrose solution?

**Q.7** A solution containing 12.5 g of a non-electrolyte substance in 175 g of water gave a boiling point elevation of 0.70 K. Calculate the molar mass of the substance. (Elevation constant for water is $K_b$ = 0.52 K kg mol$^{-1}$)

**Q.8** A solution of a non-volatile solute in water freezes at −30.0. The vapour pressure of pure water at 298 K is 23.51 mm Hg and $K_f$ for water is 1.86 degree/mol. Calculate the vapour pressure of this solution at 298 K.

**Q.9** The vapour pressure of pure benzene at 25°C is 639.7 mm Hg and the vapour pressure of a solution of non–volatile solute in benzene at the same temperature is 631.9 mm Hg.

Calculate the mole fraction of the solute and the molality of the solution. (C = 12, H = 1)

**Q.10** (i) What is osmotic pressure and how is it reached to the molecular mass of a non–volatile substance?

(ii) What advantage the osmotic pressure method has over the elevation of boiling point method for determining molecular masses?

**Q.11** State Raoults' law for solutions of nonvolatile solute in volatile solvents. Derive a mathematical expression for this law?

**Q.12** What is the molarity of a 13% solution (by weight) of sulphuric acid? Its density is 1.020 g cm$^{-1}$ (Atomic masses : H = 1, O = 16, S = 32 amu)

**Q.13** What is the molar concentration of solute particles in the human blood if the osmotic pressure is 72 atm at the body temperature of 37°C? (R = 0.0821 L atm K$^{-1}$ mol$^{-1}$)

**Q.14** Calculate the molar concentration of urea solution if it exerts an osmotic pressure of 2.45 atm at 300K. (R = 0.0821 L atm mol$^{-1}$ K$^{-1}$)

**Q.15** To 500 cm$^2$ of water, 3.0 × 10$^{-5}$ kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K$_f$ and density of water are 1.86 K kg$^{-1}$/mol and 0.997 g cm$^{-1}$ respectively.

**Q.16** How many mL of 0.1M HCl are required to react completely with 1g mixture of Na$_2$CO$_3$ and NaHCO$_3$ containing equimolar amount of two?

**Q.17** The boiling point of benzene is 353.23K. When 1.80g of a non–volatile solute was dissolved in 90g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. K$_b$ for benzene is 2.53K kg mol$^{-1}$.

**Q.18** 1.0 g of a non-electrolyte solute dissolved in 50g of benzene lowered the freezing point of benzene by 0.40K. The freezing point depression constant of benzene is 5.12 K kg mol$^{-1}$. Find the molecular mass of the solute.

**Q.19** Calculate the mass of a non–volatile solute (mol mass = 40) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

**Q.20** What is the relation between elevation in boiling point and molar heat of vapourisation?

**Q.21 (a)** The outer shells of two eggs are removed. One of the egg is placed in pure water and other is placed in saturated solution of sodium chloride. What will be observed and why?

**(b)** A decimolar solution of potassium ferrocyanide. K$_4$[Fe(CN)$_4$] is 50% dissociated at 300K. Calculate osmotic pressure of the solution. [R = 8.314 JK$^{-1}$ mol$^{-1}$]

**Q.22** Why do calculations based on lowering in freezing points of a solutions sometime give abnormal molar mass value for solutes? How may the equation for the related colligative property be modified for substance exhibiting abnormal molar mass value? A solute contains 7.45g KCl per litre of solution. It has an osmotic pressure of 4.68 atm at 300K. Calculate the degree of dissociation for KCl in this solution.

**Q.23** 0.6 mL of acetic acid (CH$_3$COOH) having density 1.06 g mL$^{-1}$, in dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C. Calculate van't Hoff factor and dissociation constant of acid.

**Q.24** Two elements A and B form compound having formula AB$_2$ and AB$_4$. When dissolved in 20g of benzene (C$_6$H$_6$) 1g of AB$_2$ lowers the freezing point by 2.3 K whereas 1.0 g of AB$_4$ lowers by 1.3K. The molar depression constant for benzene is 5.1 K kg mol$^{-1}$. Calculate atomic masses of A and B.

**Q.25** 19.5 g of CH$_2$FCOOH is dissolved in 500g water. The depression in freezing point of water observed is 1.0°C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

**Q.26** Vapour pressure of pure acetone and chloroform at 328K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition plot P$_{total}$, P$_{chloroform}$ and p$_{acetone}$ as a function of x$_{acetone}$. The experimental data observed for different compositon of mixture as:

| 100 × X$_{acetone}$ | 0 | 11.8 | 23.4 | 36.0 | 50.8 | 58.2 | 64.5 | 72.1 |
|---|---|---|---|---|---|---|---|---|
| P$_{acetone}$ | 0 | 549 | 110.1 | 202.4 | 322.7 | 405.9 | 454.1 | 521.1 |
| P$_{chloroform}$ | 632.8 | 548.1 | 469.4 | 359.7 | 257.7 | 193.6 | 161.2 | 120.7 |

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

**Q.27 (a)** Derive the relationship between relative lowering of vapour pressure and mole fraction of the volatile liquid.

**(b) (i)** Benzoic acid completely dissolves in benzene. What will be the vapour pressure of a solution containing 61g of benzoic acid per 500g benzene when the vapour pressure of the pure benzene of the temperature of experiment is 66.6 torr?

**(ii)** What would have been the vapour pressure in the absence of dissolution?

**(iii)** Derive a relationship between mole–fraction and vapour pressure of a component of an ideal solution in phase and vapour phase.

**Q.28 (a)** Which solution has higher concentration: 1 molar or 1 molal solution of the same solute. Give reasons.

**(b)** 0.5 g KCl was dissolved in 100g of water and the solution originally at 20°C, froze at –0.24°C. Calculate the percentage ionization of salt. KCl per 1000g water = 1.86.

**Q.29** How will you explain Henry's law in terms of Le Chatelier's principle and Kinetic theory of gases? or

State Henry's law for the solubility of gases in liquid. Explain it in terms of Le Chatelier's theorem.

# Exercise 2

## Single Correct Choice Type

**Q.1** Mole fraction of A vapours above the solution in mixture of A and B ($X_A$ = 0.4) will be [Given: $P_A^0$ = 100 mm Hg and $P_B^0$ = 200 mm Hg]

(A) 0.4  (B) 0.8

(C) 0.25  (D) None of these

**Q.2** The exact mathematical expression of Raoult's law is

(A) $\dfrac{P^0 - P_s}{P^0}$  (B) $\dfrac{P^0 - P_s}{P^0} = \dfrac{N}{n}$

(C) $\dfrac{P^0 - P_s}{P_s} = \dfrac{n}{N}$  (D) $\dfrac{P^0 - P_s}{P^0} = n \times N$

**Q.3** A mixture contains 1 mole of volatile liquid A ($P_A^0$ = 100 mm Hg) and 3 moles of volatile liquid B ($P_B^0$ = 80 mm Hg). If solution behaves ideally, the total pressure of the distillate is

(A) 85 mm Hg  (B) 85.88 mm H

(C) 90 mm Hg  (D) 92 mm Hg

**Q.4** Assuming each salt to be 90% dissociated, which of the following will have highest boiling point?

(A) Decimolar $Al_2(SO_4)_3$

(B) Decimolar $BaCl_2$

(C) Decimolar $Na_2SO_4$

(D) A solution obtained by mixing equal volumes of (B) and (C)

**Q.5** The vapour pressure of a solvent decreased by 10 mm of Hg when a non–volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg.

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

**Q.6** Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/mL) is

(A) $K_b$  (B) 1.20 $K_b$  (C) 1.02 $K_b$  (D) 0.98 $K_b$

**Q.7** What will be the molecular weight of $CaCl_2$ determined in its aq. solution experimentally from depression of freezing point?

(A) 111  (B) <111  (C) >111  (D) Data insufficient

**Q.8** 1.0 molal aqueous solution of an electrolyte $A_2B_3$ is 60% ionized. The boiling point of the solution at 1 atm is $K_{b(H_2O)}$ = 0.52 K kg mol$^{-1}$

(A) 274.76 K  (B) 377 K  (C) 376.4 K  (D) 374.76 K

**Q.9** The van't Hoff factor for a dilute aqueous solution of glucose is

(A) Zero  (B) 1.0  (C) 1.5  (D) 2.0

**Q.10** The correct relationship between the boiling points of very dilute solution of $AlCl_3$ ($T_1$K) and $CaCl_2$ ($T_2$K) having the same molar concentration is

(A) $T_1 = T_2$  (B) $T_1 > T_2$  (C) $T_2 < T_1$  (D) $T_2 \leq T_1$

**Q.11** A 0.001 molal solution of a complex [$MA_3$] in water has the freezing point of –0.0054°C. Assuming 100% ionization of the complex salt and $K_f$ for $H_2O$ = 1.86 km$^{-1}$, what the correct representation for the complex

(A) [$MA_8$]  (B) [$MA_7$]A  (C) [$MA_6$]$A_2$  (D) [$MA_5$]$A_3$

**Q.12** The vapour pressure of a solution of a non–volatile electrolyte B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of solute, the weight ratio of the solvent and solute are

(A) 0.15  (B) 5.7  (C) 0.2  (D) 4.0

**Q.13** The vapour pressure of a saturated solution of sparingly soluble salt ($XCl_3$) was 17.20 mm Hg at 27°C. If the vapour pressure of pure $H_2O$ is 17.25 mm Hg at 300K, what is the solubility of sparingly soluble salt $XCl_3$ in mole/litre

(A) 4.04 × 10$^{-2}$  (B) 8.08 × 10$^{-2}$

(C) 2.02 × 10$^{-2}$  (D) 4.04 × 10$^{-3}$

**Q.14** At 300K, the vapour pressure of an ideal solution containing 3 mole of A and 2 mole of B is 600 torr. At the same temperature, if 1.5 mole of A and 0.5 mole of C (non–volatile) are added to this solution the vapour pressure of solution increases by 30 torr. What is the value of $P_B^0$?

(A) 940  (B) 405  (C) 90  (D) None of these

**Q.15** The freezing point depression of a 0.1 M aq. solution of weak acid (HX) is –0.20°C. What is the value of equilibrium constant for the reaction?

HX(aq) 1H$^+$ (aq) + X$^-$ (aq) [Given: $K_f$ for water = 1.8 kg mol$^{-1}$ K and Molality = Molarity]

(A) 1.45 × 10$^{-4}$  (B) 1.35 × 10$^{-3}$

(C) 1.21 × 10$^{-2}$  (D) 1.35 × 10$^{-4}$

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**Q.16** What is the following plots represents an ideal binary mixture?

(A) Plot of $P_{total}$ v/s $1/X_B$ is linear ($X_B$ = mole fraction of 'B' in liquid phase)

(B) Plot of $P_{total}$ v/s $Y_A$ is linear ($Y_B$ = mole fraction of 'A' in vapour phase)

(C) Plot of $\dfrac{1}{P_{total}}$ v/s $Y_A$ is linear

(D) Plot of $\dfrac{1}{P_{total}}$ v/s $Y_B$ is non–linear

**Q.17** Two liquids A and B form an ideal solution. What is the vapour pressure of solution containing 2 moles of A and 3 moles of at 300K? Vapour pressure of pure liquid A ($P_A^0$) = 100 torr, Vapour pressure of pure liquid B ($P_B^0$) = 300 torr/

(A) 200 torr　　　　　(B) 140 torr

(C) 180 torr　　　　　(D) None of these

**Q.18** The van't Hoff factor for 1.0 M $Ba(NO_3)_2$ solution is 2.74. The degree of dissociation is

(A) 91.3%　　(B) 87%　　(C) 100%　　(D) 74%

## Previous Years' Questions

**Q.1** The Henry's law constant for the solubility of $N_2$ gas in water at 298 K in $1.0 \times 10^5$ atm. The mole fraction of $N_2$ in air is 0.8. The number of moles of $N_2$ from air dissolved in 10 moles of water at 298 K and 5 atm pressure is　　　　　*(2009)*

(A) $4.0 \times 10^{-4}$　　　　(B) $4.0 \times 10^{-5}$

(C) $5.0 \times 10^{-4}$　　　　(D) $4.0 \times 10^{-6}$

**Q.2** The normality of 0.3 M phosphorus acid ($H_3PO_3$) is　　　　　*(1999)*

(A) 0.1　　　(B) 0.9　　　(C) 0.3　　　(D) 0.6

**Q.3** With increase of temperature, which of these changes?　　　　　*(2002)*

(A) Molality

(B) Weight fraction of solute

(C) Fraction of solute present in water

(D) Mole fraction

**Q.4** 25 mL of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave litre value of 35 mL. The molality of barium hydroxide solution was　　　　　*(2003)*

(A) 0.07　　　(B) 0.14　　　(C) 0.28　　　(D) 0.35

**Q.5** Which of the following moles of expressing concentration is independent of temperature?　*(1988)*

(A) Molarity　　　　　(B) Molality

(C) Formality　　　　　(D) Normality

**Q.6** Two solutions of a substance (non-electrolyte) are mixed in the following manner 480 mL of 1.5M first solution + 520 mL of 1.2 M second solution. What is the molarity of the final mixture　　　　　*(2005)*

(A) 1.20 M　　　　　(B) 1.50 M

(C) 1.344 M　　　　　(D) 2.70 M

**Q.7** Increasing the temperature of an aqueous solution will cause　　　　　*(1993)*

(A) Decrease in molality

(B) Decrease in molarity

(C) Decrease in mole fraction

(D) Decrease in %w/w

**Q.8** $6.02 \times 10^{20}$ molecules of urea are present in 100 mL of its solution. The concentration of urea solution is　*(2004)*

(A) 0.02 M　　(B) 0.01 M　　(C) 0.001 M　(D) 0.1 M

[Avogadro constant, $N_A$ = $6.02 \times 10^{23}$ $mol^{-1}$]

**Q.9** To neutralize completely 20 mL of 0.1 M aqueous solution of phosphorus acid ($H_3PO_3$), the volume of 0.1M aqueous KOH solution required is　　　　*(2004)*

(A) 40 mL　　(B) 20 mL　　(C) 10 mL　　(D) 60 mL

**Q.10** A 5.2 molal aqueous solution of methyl alcohol, $CH_3OH$, is supplied. What is the mole fraction of methyl alcohol in the solution?　　　　　*(2011)*

(A) 0.100　　(B) 0.190　　(C) 0.086　　(D) 0.050

**Q.11** The density of solution prepared by dissolving 120 g of urea (mol mass = 60 u) in 1000g water is 1.15 g/mL. The molarity of this solution is　　　*(2012)*

(A) 0.50 M　　　(B) 1.78 M　　(C) 1.02 M　　(D) 2.05 M

**Q.12** Equimolar solutions in the same solvent have *(2005)*

(A) Same boiling point but different freezing point

(B) Same freezing point but different boiling point

(C) Same boiling and same freezing point

(D) Different boiling and different freezing point

**Q.13** Two liquids X and Y form an ideal solution. At 300K, vapour pressure of the solution containing 1 mol of X and 3 moles of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of X and Y in their pure states will be respectively *(2009)*

(A) 200 and 300

(B) 300 and 400

(C) 400 and 600

(D) 500 and 600

**Q.14** The vapour pressure of water at 20°C is 17.5 mm Hg. If 18g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C the vapour pressure of the resulting solution will be *(2005)*

(A) 15.750 mm Hg

(B) 16.500 mm Hg

(C) 17.325 mm Hg

(D) 17.675 mm Hg

**Q.15** A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be *(2007)*

(A) 350      (B) 300      (C) 700      (D) 360

**Q.16** Which of the following liquid pair shows a positive deviation from Raoult's law *(2004)*

(A) Water–nitric acid

(B) Benzene–methanol

(C) Water–hydrochloric acid

(D) Acetone–chloroform

**Q.17** A 5.25% solution of a substance is isotonic with 1.5% solution of urea (molar mass = 60g mol⁻¹) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm⁻³, molar mass of the substance will be *(2007)*

(A) 90.0 g mol⁻¹

(B) 115.0 g mol⁻¹

(C) 105.0 g mol⁻¹

(D) 210.0 g mol⁻¹

**Q.18** Value of gas constant R is *(2002)*

(A) 0.082 litre atm

(B) 0.987 cal mol⁻¹K⁻¹

(C) 8.3 J mol⁻¹ K⁻¹

(D) 83 erg mol⁻¹ K⁻¹

**Q.19** During depression of freezing point in a solution the following are in equilibrium *(2003)*

(A) Liquid solvent, solid solvent

(B) Liquid solvent, solid solute

(C) Liquid solute, solid solute

(D) Liquid solute, solid solvent

**Q.20** The degree of dissociation ($\alpha$) of a weak electrolyte, $A_xB_y$ is related to van't Hoff factor (i) by the expression *(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) $\alpha = \dfrac{x+y+1}{i-1}$

**Q.21** At 80°C, the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80°C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg) *(2008)*

(A) 52 mol percent

(B) 34 mol percent

(C) 48 mol percent

(D) 50 mol percent

**Q.22** If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water $(\Delta T_f)$, when 0.01 mol of sodium sulphate is dissolved in 1 kg of water, is ($K_f$ = 1.86 K kg mol⁻¹) *(2010)*

(A) 0.0372 K

(B) 0.0558 K

(C) 0.0744 K

(D) 0.0186 K

**Q.23** 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 = 62g mol⁻¹]

(A) 204.30g

(B) 400.00 g

(C) 304.60 g

(D) 804.32g

**Q.24** $K_f$ for water is 1.86 K kg mol-1. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to −2.8°C?     **(2012)**

(A) 72g     (B) 93g     (C) 39g     (D) 27g

**Q.25** Consider separate solutions of 0.500 M $C_2H_5OH_{(aq)}$ , 0.100M $Mg_3(PO_4)_{2(aq)}$ 0.250 M $KBr_{(aq)}$ and 0.125 M $Na_3PO_{4(aq)}$ at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes?     **(2014)**

(A) They all have the same osmotic pressure.

(B) 0.100 M $Mg_3(PO_4)_{2(aq)}$ has the highest osmotic pressure.

(C) 0.125 M $Na_3PO_{4(aq)}$ has the highest osmotic pressure.

(D) 0.500 M $C_2H_5OH_{(aq)}$ has the highest osmotic pressure.

**Q.26** The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone a 20°C, its vapour pressure was 183 torr. The molar mass (g mol⁻¹) of the substance is:     **(2014)**

(A) 32     (B) 64     (C) 128     (D) 488

**Q.27** 18 g glucose $(C_6H_{12}O_6)$ is added to 178.2 g water. The vapor pressure of water (in torr) for this aqueous solution is.     **(2016)**

(A) 76.0     (B) 752.4     (C) 759.0     (D) 7.6

# JEE Advanced/Boards

## Exercise 1

**Q.1** At 25ºC, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of $CH_3OH$ in a solution in which the (partial) vapour pressure of $CH_3OH$ is 23.0 torr at 25ºC?

**Q.2** The vapour pressure of pure liquid solvent A is 0.80 atm. When a non–volatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of components B in the solution?

**Q.3** The vapour pressure of pure water at 26ºC is 25.21 torr. What is the vapour pressure of a solution which contains 20.0 glucose, $C_4H_{12}O_6$, in 70g water?

**Q.4** The vapour pressure of pure water at 25ºC is 23.76 torr. The vapour pressure of a solution containing 5.40 g of a non–volatile substance in 90.0g water is 23.32 torr. Compute the molecular weight of the solute.

**Q.5** What weight of the non–volatile solute, urea needs to be dissolved in 100g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

**Q.6** When 10.6 g of a non–volatile substance is dissolved in 740g of ether, its boiling point is raised 0.284ºC. What is the molecular weight of the substance? Molal boiling point constant for ether is 2.11ºC kg/mol.

**Q.7** A solution containing 3.24 of a nonvolatile nonelectrolyte and 200g of water boils at 100.130ºC at 1atm. What is the molecular weight of the solute? ($K_b$ for water 0.513ºC/m).

**Q.8** The molecular weight of an organic compound is 58.0 g/mol. Compute the boiling point of a solution containing 24.0 g of the solute and 600g of water, when the barometric pressure is such that pure water boils at 99.725ºC.

**Q.9** An aqueous solution of a non–volatile solute boils at 100.17ºC. At what temperature will this solution freeze? [$K_f$ for water 1.86ºC/m]

**Q.10** Find the freezing point of a glucose solution whose osmotic pressure at 25ºC is found to be 30 atm. $K_f$(water) = 1.86 kg/mol K.

**Q.11** The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373K. Calculate molality and mole fraction of solute.

**Q.12** The vapour pressure of pure benzene at 25ºC is 639.7 mm of Hg and the vapour pressure of a solution of a solute in $C_6H_6$ at the same temperature is 631.7mm of Hg. Calculate molality of solution.

**Q.13** The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile non-

electrolyte solid weighing 2.175 g is added to 39.0 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?

**Q.14** The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.

**Q.15** Benzene and toluene form two ideal solutions A and B at 313K. Solution A (total pressure $P_A$) contains equal moles of toluene and benzene. Solution B contain equal masses of both (total pressure $P_B$). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313K. Calculate the value of $P_A/P_B$.

**Q.16** Sea water is found to contain 5.85% NaCl and 9.50% MgCl by weight of solution. Calculate its normal boiling point assuming 80% ionization for NaCl and 50% ionization of $MgCl_2$ [$K_b(H_2O)$ = 0.51 kg mol$^{-1}$ K].

**Q.17** The latent heat of fusion of ice is 80 calories per gram at 0°C. What is the freezing point of a solution of KCl in water containing 7.45 grams of solute in 500 grams of water, assuming that the salt is dissociated to the external of 95%?

**Q.18** A complex is represented as $CoCl_3 \cdot xNH_3$. Its 0.1 molal solution in aq. solution shows $\Delta T_f$ = 0.558°C. $K_f$ for $H_2O$ is 1.86 K mol$^{-1}$ kg. Assuming 100% ionization of complex and coordination no. of Co is six, calculate formula of complex.

**Q.19** The molar volume of liquid benzene (density = 0.877 g mL$^{-1}$) increases by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density = 0.867 mL$^{-1}$) increases by a factor of 7720 at 20°C. Solution of benzene and toluene has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in vapour above the solution.

**Q.20** At 100°C, benzene and toluene have vapour pressure of 1375 and 558 torr respectively. Assuming these two form an ideal binary solution, calculate the composition of the solution that boils at 1 atm and 100°C. What is the composition of vapour issuing at these conditions?

**Q.21** At 300K, the solution of glucose in water of concentration 0.01 M and 0.001M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? Calculate the magnitude of this applied pressure.

**Q.22** At 10°C, the osmotic pressure of urea solution is 500mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.

**Q.23** The freezing point of a solution containing 0.2g of acetic acid in 20.0 g of benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene.

**Q.24** 0.85% aqueous solution of $NaNO_3$ is apparently 90% dissociated at 27°C. Calculate its osmotic pressure. (R = 0.082 $l$ atm K$^{-1}$ mol$^{-1}$).

**Q.25** A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.

**Q.26** Calculate the boiling point of a solution containing 0.61g of benzoic acid in 50g of carbon disulphide assuming 84% dimerization of the acid. The boiling point and Kb of $CS_2$ are 46.2°C and 2.3 K kg mol$^{-1}$, respectively.

**Q.27** At 25°C, 1 mol of A having a vapour pressure of 100 torr and 1 mol of B having a vapour pressure of 300 torr were mixed. The vapour at equilibrium is removed, condensed and the condensate is heated back to 25°C. The vapours now formed are again removed, recondensed and analysed. What in the mole fraction of A in this condensate?

**Q.28** Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20 × 10$^{-3}$ kg phenol in 1kg of benzene has its freezing point depressed by 0.69K. Calculate the fraction of phenol that has dimerised K for benzene = 5.12 kg mol$^{-1}$ K.

**Q.29** 30 mL of $CH_3OH$ (d = 0.7980 gm cm$^{-3}$) and 70 mL of $H_2O$ (d = 0.9984 gm cm$^{-3}$) are mixed at 25°C to form a solution of density 0.9575 gm cm$^{-3}$. Calculate the freezing point of the solution. $K_f$ ($H_2O$) is 1.86 kg mol$^{-1}$ K. Also calculate its molarity.

## Exercise 2

### Single Correct Choice Type

**Q.1** For an ideal binary liquid solution with $P_A^0 > P_B^0$, which relation between $X_A$ (mole fraction of A in liquid phase) and $Y_A$ (mole fraction of A in vapour phase) is correct?

(A) $Y_A < Y_B$           (B) $X_A > X_B$

(C) $\dfrac{Y_A}{Y_B} > \dfrac{X_A}{X_B}$      (D) $\dfrac{Y_A}{Y_B} < \dfrac{X_A}{X_B}$

**Q.2** Which of the following aqueous solution will show maximum vapour pressure at 300K?

(A) 1 M NaCl

(B) 1 M $CaCl_2$

(C) 1 M $AlCl_3$

(D) 1 M $C_{12}H_{22}O_{11}$

**Q.3** At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by $P_{Total}$ = 120 – 75$X_B$ hence, vapour pressure of pure A and B respectively (in Torr) are

(A) 120, 75

(B) 120, 95

(C) 120, 45

(D) 75, 45

**Q.4** A liquid mixture having composition corresponding to point z in the figure shown in subjected to distillation at constant pressure. Which of the following statement is correct about the process



$x_A=0$    mole    $x_A=1$
$y_A=0$  fraction  $y_A=1$
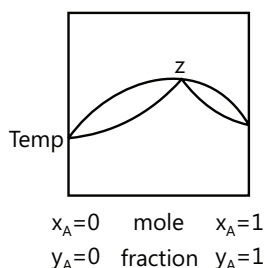
(A) The composition of distillate differs from the mixture

(B) The boiling point goes on changing

(C) The mixture has highest vapour pressure than for any other composition

(D) Composition of an azeotrope alters on changing the external pressure

**Q.5** The following graph represents variation of boiling point with composition of liquid and vapour of binary liquid mixture. The graph is plotted at constant pressure. Which of the following statement(s) is incorrect. Here X and Y stands for mole fraction in liquid and vapour phase respectively

$$\Rightarrow t = \sqrt{\frac{2L}{\omega^2 R}}$$

(A) $X_{benzene}$ = 0.5 and $Y_{toluene}$ = 0. 2

(B) $X_{toluene}$ = 0.3 and $Y_{benzene}$ = 0. 6

(C) $X_{benzene}$ = 0.3 and $Y_{toluene}$ = 0. 4

(D) $X_{benzene}$ = 0.7 and $Y_{toluene}$ < 0. 3

**Q.6** Which of the following represent correctly the changes in thermodynamic properties during the formation of 1 mol of an ideal binary solution
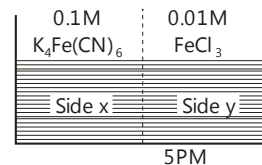


(A) $J\ mol^{-1}$

Mole fraction
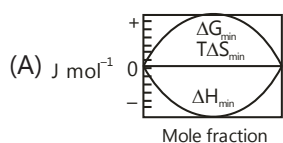
(B) $\tan\theta = \dfrac{v^2}{Rg} = \dfrac{(10)^2}{(10)(10)} = 1$

(C) $\theta = \tan^{-1}(1) = 45°$

(D) $\dfrac{dv}{dt} = a$

**Q.7** $FeCl_3$ on reaction with $K_4[Fe(CN)_6]$ in aqueous solution given blue colour. These are separated by a semipermeable membrane AB as shown. Due to osmosis there is



| 0.1M | 0.01M |
|------|-------|
| $K_4Fe(CN)_6$ | $FeCl_3$ |

Side x    Side y

5PM

(A) Blue colour formation in side X

(B) Blue colour formation in side Y

(C) Blue colour formation in both of the sides X and Y

(D) No blue colour formation

**Multiple Correct Choice Type**

**Q.8** Acetone and carbon disulphide form binary liquid solution showing positive deviation from Raoult's law. The normal boiling point ($T_b$) of pure acetone is less than that of pure $CS_2$. Pick out the incorrect statement among the following

(A) Boiling temperature of mixture is always less than boiling temperature of acetone

(B) Boiling temperature of Azetropic mixture is always less than boiling temperature of acetone

(C) When a small amount of $CS_2$ (less volatile component) is added to excess of acetone boiling point of resulting mixture increases

(D) A mixture of $CS_2$ and $CH_3COCH_3$ can be completely separated by simple fractional distillation.

**Q.9** Which of the following would be equal to zero when the liquid pairs form an ideal solution

(A) $\Delta H$      (B) $\Delta S$      (C) $\Delta G$      (D) $\Delta V$

**Q.10** For a non–volatile solute

(A) The vapour pressure of solute is zero

(B) Vapour pressure of solution = Vapour pressure of pure solvent

(C) Vapour pressure of solution = Vapour pressure of solvent in solution

(D) All of the above

**Q.11** A difference between diffusion and osmosis is

(A) A semipermeable membrane is required for osmosis while diffusion requires no semipermeable membrane

(B) In osmosis movement of molecules is only in one direction whereas in diffusion movement is on both sides

(C) In osmosis only the solvent moves while in diffusion both solute and solvent move

(D) None of the above

**Q.12** Which of the following statement is/are correct?

(A) The freezing point of water is depressed by the addition of glucose

(B) The degree of dissociation of a weak electrolyte decrease as its concentration decreases

(C) Energy is released when a substance dissolves in water provided that the hydration energy of the substance is more than its lattice energy

(D) If two liquids that form an ideal solution are mixed, the change in entropy is positive

**Q.13** Which of the following gases are highly soluble in water

(A) HCl      (B) $SO_2$      (C) $NH_3$      (D) $H_2$

**Q.14** Which of the following would be equal to zero when the liquid pairs form an ideal solution.

(A) $\Delta H$      (B) $\Delta S$      (C) $\Delta G$      (D) $\Delta V$

**Q.15** Two miscible liquids A and B having vapour pressure in pure state $P_A^0$ and $P_B^0$ are mixed in mole reaction $X_A$ and $X_B$ to get a mixture having total vapour pressure of mixture $P_M$. Which of the following relation are correct?

(A) $X_A = \dfrac{P_M - P_B^0}{P_A^0 - P_B^0}$

(B) $\dfrac{X_{A(\ell)}}{X'_{A(V)}} = \dfrac{P_M}{P_A^0}$

(C) $\dfrac{X_{A(\ell)}}{X'_{A(V)}} = \dfrac{P_M}{P_B^0}$

(D) All of these

**Q.16** Which relations are not correct for aqueous dilute solution of $K_3PO_4$ if its degree of dissociation is $\alpha$?

(A) $\dfrac{\Delta P}{P^o} = \dfrac{\text{Molality} \times 18 \times (1 + 3\alpha)}{1000}$

(B) $\dfrac{\Delta P}{P^o} = \dfrac{\pi_{obs} \times 18 \times (1 + 3\alpha)}{RT \times 1000}$

(C) $\dfrac{\Delta P}{P^o} = \dfrac{\Delta T_{fobs} \times 18}{K_f \times 1000}$

(D) Mw of $K_2PO_4$ = $Mw_{obs} \times (1 + 3\alpha)$

**Q.17** Which of the following is/are true?

(A) For the same solution, elevation in boiling point = depression in freezing point

(B) The Van't Hoff factor for a dilute solution of $BaCl_2$.

(C) The elevation in boiling point is due to increase in vapour pressure.

(D) The depression in freezing point is due to decrease in vapour pressure.

**Q.18** Which pairs of liquids on mixing is/are expected to show no net volume change and no heat effect?

(A) Acetone and ethanol

(B) Chloro benzene and bromo benzene

(C) Chloroform and benzene

(D) n–Butyl chloride and n–butyl bromide

**Assertion Reasoning Type**

**Q.19 Statement-I:** Addition of ethylene glycol (non–volatile) to water lowers the freezing point of water hence used as antifreezing

**Statement-II:** Heat must be removed from the water to make it freeze.

(A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I

(B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I

(C) Statement-I is true, statement-II is false.

(D) Statement-I is false, statement-II is true

**Q.20 Statement-I:** The freezing of water is an endothermic process.

**Statement-II:** Heat must be removed from the water to make it freeze.

(A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I.

(B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I.

(C) Statement-I is true, statement-II is false.

(D) Statement-I is false, statement-II is true

## Comprehension Type

The various relations between colligative properties and molecular mass are applicable only to solutions of non–electrolytes and in dilute solutions. Out of various colligative properties osmotic pressure measurement is especially suitable for the determination of molecular masses of proteins whereas freezing point depression and other colligative properties are too small. Certain solutes which dissociate or associate in solution affect the colligative property and hence molecular mass determination also. In case of association observed molecular mass is more than normal the correction factor i < 1. For dissociation of solute i > 1 and observed molecular mass is less than the normal molecular mass

**Q.21** Which of the following 0.1 m aqueous solution will have the lowest freezing point?

(A) $Al_2(SO_4)_3$        (B) $C_6H_{12}O_6$

(C) KI        (D) $C_{12}H_{22}O_{11}$

**Q.22** Correction factor for 0.1M ideal solution is

(A) 0.1        (B) 1        (C) 0.01        (D) 2 > 1

**Q.23** The Van't Hoff factor for 0.1M $Ba(NO_3)_2$ solution is 2.74. The degree of dissociation is

(A) 91.3%        (B) 87%        (C) 100%        (D) 74%

**Q.24** Which one of the following statements gives below concerning properties of a solution describe a colligative effect?

(A) Boiling point of pure water increase by addition of EtOH

(B) Vapour pressure of pure water decrease by addition of $HNO_3$

(C) Vapour pressure of pure benzene decrease by addition of naphthalene

(D) Boiling point of pure benzene increase by addition of toluene

**Q.25** After adding a solute, freezing point of water decreases to –0.186°C. What is the value of ΔT? ($k_b$ = 0.521; $k_f$ = 1.86)

(A) 0.521        (B) 0.0521

(C) 1.86        (D) 0.0186

## Match the Columns

**Q.26** $P_A$ = partial pressure of components A in liquid mixture. $P_A^0$ = vapour pressure of A, $\chi_A$ = mole fraction of A in liquid

| Column I | Column II |
|---|---|
| (A) $C_2H_5OH + H_2O$ | (p) Azeotropic mixture |
| (B) $C_2H_2Br + C_2H_5I$ | (q) Obeys Raoult's law |
| (C) $P_A = X_A P_A^0$ | (r) Non–ideal solution with positive deviation |
| (D) $H_2O + H_2SO_4$ | (s) Non–ideal solution with negative deviation |
| | (t) Ideal solution |

**Q.27** Match the following

| Column I | Column II |
|---|---|
| (A) Urea, glucose, fructose | (p) 1 : 0.8 : 1 |
| (B) NaCl, $MgCl_2.K_2SO_4$ | (q) 1 : 2 : 1 |
| (C) $Al_2(SO_4)_3$, $Na_3PO_4$, $K_3r[Fe(CN)_6]$ | (r) 1 : 1 : 1 |
| (D) Glucose, NaCl, $CaCl_2$ | (s) 2 : 3 : 3 |

**Q.28**

| Column I | Column II |
|---|---|
| (A) ppm | (p) Van't Hoff factor |
| (B) $\Delta T_b$ | (q) Molal depression |
| (C) $K_f$ | (r) Elevation in boiling point |
| (D) i | (s) $\dfrac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$ |

# Previous Years' Questions

**Q.1** An azeotropic solution of two liquids has boiling point lower than either of them when it        *(1981)*

(A) Shows negative deviation from Raoult's law

(B) Shows no deviation from Raoult's law

(C) Shows positive deviation from Raoult's law

(D) Is saturated

**Q.2** Which of the following 0.1M aqueous solution will have the lowest freezing point? *(1989)*

(A) Potassium sulphate   (B) Sodium chloride

(C) Urea                 (D) Glucose

**Q.3** During depression of freezing point in a solution the following are in equilibrium *(2003)*

(A) Liquid solvent, solid solvent

(B) Liquid solvent, solid solute

(C) Liquid solute, solid solute

(D) Liquid solute, solid solvent

**Q.4** The freezing point (in °C) of solution containing 0.1 g of $K_3[Fe(CN)_6]$ (mol. wt. 329) in 100 g of water ($K_f$ = 1.86 K kg mol$^{-1}$) is *(2011)*

(A) $-2.3 \times 10^{-2}$        (B) $-5.7 \times 10^{-2}$

(C) $-5.7 \times 10^{-3}$        (D) $-1.2 \times 10^{-2}$

**Paragraph 3**

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti–freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given, freezing point depression constant of water ($k_f^{water}$) = 1.86 K kg mol$^{-1}$

freezing point depression constant of ethanol ($k_f^{ethanol}$) = 2.0 K kg mol$^{-1}$

Boiling point elevation constant of water ($k_b^{water}$) = 0.52 K kg mol$^{-1}$

Boiling point elevation constant of water ($k_f^{ethanol}$) = 1.2 K kg mol$^{-1}$

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol$^{-1}$

Molecular weight of ethanol = 46 g mol$^{-1}$

In answering the following questions, consider the solution to be ideal dilute solution and solute to be non–volatile and non–dissociative. *(2008)*

**Q.5** The freezing point of the solution M is

(A) 268.7 K              (B) 268.5 K

(C) 234.2 K              (D) 150.9 K

**Q.6** The vapour pressure of the solution M is

(A) 39.3 mm Hg           (B) 36.0 mm Hg

(C) 29.6 mm Hg           (D) 28.8 mm Hg

**Q.7** Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is

(A) 380.4 K              (B) 376.2 K

(C) 375.5 K              (D) 354.7 K

**Q.8** Following statement is true only under some specific conditions. Write the condition, for it "Two volatile and miscible liquids can be separated by fractional distillation into pure components".

**Q.9** An organic compound ($C_xH_{2y}O_y$) was burnt with twice the amount of oxygen needed for complete combustion to $CO_2$ and $H_2O$. The hot gases when cooled to 0°C and 1 atm pressure, measured 2.24 L. The water collected during cooling weigh 0.9g. The vapour pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50g of the organic compound are dissolved in 1000g of water. Give the molecular formula of the organic compound. *(1983)*

**Q.10** The vapour pressure of ethanol and methanol are 44.5 and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by the mixing 60g of ethanol with 40g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. *(1986)*

**Q.11** The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non–volatile, non–electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of solution is 600 mm Hg. What is the molecular weight of the solid substance? *(1990)*

**Q.12** The degree of dissociation of Ca $(NO_3)_2$ in a dilute aqueous solution, containing 7.0g of the salt per 100g of water at 100°C is 70%. If the vapour–pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution. **(1991)**

**Q.13** Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon : 42.86%, hydrogen : 2.40%, nitrogen : 16.67% and oxygen : 38.07%,

**(i)** Calculate the empirical formula of the minor product.

**(ii)** When 5.5g of the minor product is dissolved in 45g of benzene, the boiling point of the solution is 1.84°C higher than that of pure benzene. Calculate the molar mass of the minor product then determine its molecular and structural formula. (Molal boiling point elevation constant of benzene is 2.53 K kg mol⁻¹). **(1999)**

**Q.14** The vapour pressure of two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 moles of (A) is mixed with 12 moles of (B). However, as soon as (B) is added, (A) starts polymerizing into a completely insoluble solid. The polymerization follows first order kinetic. After 100min, 0.525 mole of a solute is dissolved which arrests the polymerization completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerization and ideal behavior for the final solution. **(2001)**

**Q.15** Consider the three solvents of identical molar masses. Match their boiling point with their $k_b$ values **(2003)**

| Solvents | Boiling point | $k_b$ values |
|---|---|---|
| X | 100°C | 0.92 |
| Y | 27°C | 0.63 |
| Z | 283°C | 0.53 |

**Q.16** When 20 g of naphthoic acid $(C_{11}H_8O_2)$ is dissolved in 50 g of benzene (Kf = 1.72 K kg mol⁻¹), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is **(2007)**

(A) 0.5     (B) 1     (C) 2     (D) 3

**Paragraph for Question Nos. 17 to 19**

Properties such as boiling point, freezing point and vapor pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given: Freezing point depression constant of water $\left(K_f^{water}\right)$ = 1.86 K kg mol⁻¹ Freezing point depression constant of ethanol $\left(K_f^{ethanol}\right)$ = 2.0 K kg mol⁻¹ Boiling point elevation constant of water $\left(K_b^{water}\right)$ = 0.52 K kg mol⁻¹

Boiling point elevation constant of ethanol $\left(K_b^{ethanol}\right)$ = 1.2 K kg mol⁻¹

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative. **(2008)**

**Q.17** The freezing point of the solution M is

(A) 268.7 K     (B) 268.5 K

(C) 234.2 K     (D) 150.9 K

**Q.18** The vapour pressure of the solution M

(A) 39.3 mm Hg     (B) 36.0 mm Hg

(C) 29.5 mm Hg     (D) 28.8 mm Hg

**Q.19** Water is added to the solution M such that the fraction of water in the solution becomes 0.9. The boiling point of this solution is

(A) 380.4 K     (B) 376.2 K

(C) 375.5 K     (D) 354.7 K

**Q.20** The Henry's law constant for the solubility of $N_2$ gas in water at 298 K is 1.0 × 10⁵ atm. The mole fraction of $N_2$ in air is 0.8. The number of moles of $N_2$ from air dissolved in 10 moles of water at 298 K and 5 atm pressure is **(2009)**

(A) 4.0 × 10⁻⁴     (B) 4.0 × 10⁻⁵

(C) 5.0 × 10⁻⁴     (D) 4.0 × 10⁻⁶

**Q.21** The freezing point (in °C) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (Mol. Wt. 329) in 100 g of water $(K_f$ = 1.86 K kg mol⁻¹) is **(2011)**

(A) -2.3 × 10⁻²     (B) -5.7 × 10⁻²

(C) -5.7 × 10⁻³     (D) -1.2 × 10⁻²

**Q.22** For a dilute solution containing 2.5 g of a non-volatile non- electrolyte solute in 100 g of water, the elevation in boiling point at 1atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapor pressure (mm of Hg) of the solution is (take $K_b$ = 0.76 K kg mol$^{-1}$)

*(2012)*

(A) 724    (B) 740    (C) 736    (D) 718

**Q.23** If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is − 0.0558°C, the number of chloride(s) in the coordination sphere of the complex is [$K_f$ of water = 1.86 K kg mol$^{-1}$]

**Q.24** The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm$^{-3}$. The ratio of the molecular weights of the solute and solvent $\left( \dfrac{MW_{solute}}{MW_{solvent}} \right)$, is

*(2016)*

**Q.25** Mixture(s) showing positive deviation from Raoults law at 35°C is (are)    *(2016)*

(A) Carbon tetrachloride + methanol

(B) Carbon disulphide + acetone

(C) Benzene + toluene

(D) Phenol + aniline

# PlancEssential Questions

## JEE Main/Boards

### Exercise 1

| | | |
|---|---|---|
| Q.2 | Q.4 | Q.9 |
| Q.14 | Q.29 | |

### Exercise 2

| | | |
|---|---|---|
| Q.2 | Q.4 | Q.14 |
| Q.17 | | |

### Previous Years' Questions

| | | |
|---|---|---|
| Q.6 | Q.9 | Q.11 |
| Q.16 | Q.17 | |

## JEE Advanced/Boards

### Exercise 1

| | | |
|---|---|---|
| Q.6 | Q.10 | Q.16 |
| Q.20 | Q.21 | Q.25 |

### Exercise 2

| | | |
|---|---|---|
| Q.6 | Q.7 | Q.12 |
| Q.15 | Q.17 | Q.25 |
| Q.28 | | |

### Previous Years' Questions

| | |
|---|---|
| Q.1 | Q.13 |

# Answer Key

## JEE Main/Boards

### Exercise 1

**Q.1** 4.9 gm | **Q.2** 0.89 | **Q.3** (i) 0.52m, (ii) 0.99

**Q.6** 0.2121 m | **Q.7** 53.06g mol$^{-1}$ | **Q.8** 23.44 mm Hg

**Q.9** 0.988; 0.156 m | **Q.12** 1.35 mol/litre; 1.52 mol/kg | **Q.13** 0.283 mol/L

**Q.14** 0.099 mol L$^{-1}$ | **Q.15** 0.23 K

**Q.16** 158.9 mL of 0.1 M HCl | **Q.17** 57.5 g mol$^{-1}$ | **Q.18** 256 g mol$^{-1}$

**Q.19** 10 g | **Q.21** (b) 7.389 atm

**Q.22** Degree of dissociation = 90% | **Q.23** 18.6 × 10$^{-4}$

**Q.24** Atomic mass of A = 25.59; B = 42.64 | **Q.25** 1.0753; 30.68 × 10$^{-4}$ | **Q.28** (b) 92%

### Exercise 2

**Single Correct Choice Type**

**Q.1** C | **Q.2** C | **Q.3** A | **Q.4** A | **Q.5** C | **Q.6** D

**Q.7** B | **Q.8** D | **Q.9** B | **Q.10** B | **Q.11** C | **Q.12** B

**Q.13** A | **Q.14** C | **Q.15** B | **Q.16** C | **Q.17** D | **Q.18** B

### Previous Years' Questions

**Q.1** A | **Q.2** D | **Q.3** C | **Q.4** A | **Q.5** B | **Q.6** C

**Q.7** B | **Q.8** B | **Q.9** A | **Q.10** C | **Q.11** D | **Q.12** C

**Q.13** C | **Q.14** C | **Q.15** A | **Q.16** B | **Q.17** D | **Q.18** C

**Q.19** A | **Q.20** A | **Q.21** D | **Q.22** B | **Q.23** D | **Q.24** B

**Q.25** A | **Q.26** B | **Q.27** B

## JEE Advanced/Boards

### Exercise 1

**Q.1** 0.24 | **Q.2** 0.25 | **Q.3** 24.5 torr

**Q.4** 57.24 g/mol | **Q.5** 111.1 g, 18.52 molal | **Q.6** 106 g/molal

**Q.7** 64.0 g/mol | **Q.8** 100.079°C | **Q.9** −0.62°C

**Q.10** T = -2.28°C | **Q.11** 0.741m, 0.013 | **Q.12** 0.162 m

**Q.13**. 65.25 | **Q.14** 17.38 | **Q.15** 0.964

**Q.16** $T_b$ = 101.9°C | **Q.17** $T_f$ = −0.73°C | **Q.18** [Co(NH$_3$)Cl]Cl$_2$

**Q.19** 0.73 | **Q.20** $x_B$ = 0.2472, $y_b$ = 0.4473

**Q.21** P = 0.2217 atm should be applied

**Q.22** ($V_{total}$ = 5.$V_{original}$)

**Q.23** 94.5%

**Q.24** 4.64 atm

**Q.25** 0.95; 1.95

**Q.26** 46.33°C

**Q.27** x = 0.1

**Q.28** a = 0.7333

**Q.29** −19.91°C, 7.63M

## Exercise 2

**Single Correct Choice Type**

**Q.1** C     **Q.2** D     **Q.3** C     **Q.4** D     **Q.5** B     **Q.6** C

**Q.7** D

**Multiple Correct Choice Type**

**Q.8** A, C, D     **Q.9** A, D     **Q.10** A, C     **Q.11** A, B, C     **Q.12** A, C, D     **Q.13** A, B, C

**Q.14** A, D     **Q.15** A, B     **Q.16** A, C, D     **Q.17** B, D     **Q.18** B, D

**Assertion Reasoning Type**

**Q.19** C     **Q.20** D

**Comprehension Type**

**Q.21** A     **Q.22** B     **Q.23** B     **Q.24** C     **Q.25** B

**Match the Columns**

**Q.26** A → p, r; B → q, t; C → q, t; D → p, s

**Q.27** A → r; B → s; C → p; D → q

**Q.28** A → s; B → r; C → q; D → p

## Previous Years' Questions

**Q.1** C     **Q.2** A     **Q.3** A     **Q.4** A     **Q.5** D     **Q.6** A

**Q.7** B     **Q.8** Condition     **Q.9** $C_5H_{10}O_{11}$     **Q.10** 0.657     **Q.11** 65.25     **Q.12** 746.32

**Q.13** 168     **Q.14** $1.005 \times 10^{-4}$ min$^{-1}$     **Q.15** Subjective     **Q.16** A     **Q.17** D

**Q.18** B     **Q.19** B     **Q.20** A     **Q.21** A     **Q.22** A     **Q.23** 3

**Q.24** 9     **Q.25** A,B

# Solutions

## JEE Main/Boards

## Exercise 1

**Sol 1:** We have

Molecular mass of $H_2SO_4 = 98g$

Let weight be w

Then moles $n = \dfrac{w}{98}$

Now $\dfrac{n}{V} = 0.2$

$\dfrac{w \times 1000}{98 \times 250} = 0.2$

w = 4.9 g

**Sol 2:** Molecular wt of ethanol = 46 gm

Moles of ethanol $n_1 = \dfrac{23}{46} = 0.5$

Molecular mass of water = 18 gm

Moles of water, $n_2 = \dfrac{72}{18} = 4$

$X_e = \dfrac{n_1}{n_1 + n_2} = \dfrac{0.5}{4 + 0.5} = 0.11$

$X_w = \dfrac{n_2}{n_1 + n_2} = \dfrac{4}{4 + 0.5} = 0.89$

**Sol 3:** Moles of glucose, $n_1 = \dfrac{2.82}{180} = 0.0152$

(i) Molality $= = \dfrac{n_1 \times 1000}{30} = \dfrac{0.0156}{30} \times 1000 = 0.52$

(ii) moles of water, $n_2 = \dfrac{30}{18} = 1.66$

$X_g = \dfrac{0.0152}{0.0152 + 1.66} \approx 0.01$

$X_w = 1 - X_g = 0.99$

**Sol 5:** $\Delta T_b = k_b m$

$\pi = CRT$

$\therefore \dfrac{\pi}{\Delta T_b} = \dfrac{CRT}{k_b m} = \dfrac{n}{Vk_b.n} RT. w_s = \dfrac{RT}{k_b}.\delta_s$

Where $\delta_s$ = density of solute $= \dfrac{W_s}{V}$

$\therefore \pi = \dfrac{RT\delta_s}{k_b} \Delta T_0$

**Sol 6:** We have,

$\pi = CRT$

$\Rightarrow C = \dfrac{\pi}{RT} = \dfrac{4.85}{0.0821 \times 293} = 0.201 \text{ m}$

Weight of solvent of solute $= 0.201 \times 1 = 0.201$

Weight of solvent $= 1015 - 68.95g = 946.04g$

$\therefore$ Molality $= \dfrac{0.201}{946.04} \times 1000$

Molality $= 0.2121m$

**Sol 7:** We have

$\Delta T_b = k_b m \Rightarrow m = \dfrac{\Delta T_b}{k_b} = \dfrac{0.7}{0.52}$ ; m = 1.346m

$m = \dfrac{n}{w_s}$

$n = 1.346 \times |75|1000; n = 0.235$

$n = \dfrac{w}{m} \Rightarrow M = \dfrac{w}{n} = \dfrac{12.5}{0.235}$

M = 53.6 g mol$^{-1}$

**Sol 8:** We have,

$\Delta T_f = 0.3^0 \text{ C} = k_f m$

$m = \dfrac{0.3}{1.86} = 0.161m$

Now we have,

$\dfrac{P_0 - P}{P_0} = X_a$

$m = \dfrac{n}{w_s} \Rightarrow w_s = \dfrac{n}{m}$

$n_s = \dfrac{w_s}{M_s} = \dfrac{n}{M_s}$

$X_a = \dfrac{n}{n_s + n} = \dfrac{n}{\dfrac{n}{mM_s} + n} = \dfrac{1}{1 + \dfrac{1}{mM_s}} = \dfrac{1}{1 + \dfrac{1}{\dfrac{18 \times 0.161}{1000}}}$

$X_a = 2.88 \times 10^{-3}$

Now, $P_0 = 23.51 \, mmHg$

$\dfrac{23.51 - P}{23.51} = 2.88 \times 10^{-3}$

$\Rightarrow P = 23.44 \, mmHg$

**Sol 9:** $X_a = \dfrac{P_0 - P}{P_0}$

$\dfrac{639.7 - 631.9}{639.7} = 1.22 \times 10^{-2}$

Also, from previous question.

$X_a = \dfrac{1}{1 + \dfrac{1}{mM_s}}$, $M_s = 78 \, g$

$1 + \dfrac{1}{mM_s} = \dfrac{1}{X_a}$

$\dfrac{1}{mM_s} = \dfrac{1}{X_a} - 1 = \dfrac{1 - X_a}{X_a}$

$mM_s = \dfrac{X_a}{1 - X_a}$

$m = \dfrac{X_a}{(1 - X_a).M_s}$

By substituting the values,

We get m = 0.156m

**Sol 10:** (i) Osmotic pressure is the excess pressure which must be applied to a given solution in order to increase it's vapour pressure until it becomes equal to that of the solution.

$M_0 = \dfrac{wRT}{\pi V}$; w = weight of solute

$\pi$ = osmotic pressure

(ii) Osmotic pressure has a relatively large magnitude and is easy to measure compared to $\Delta T_b$.

**Sol 12:** For every 1 kg of solution,

wt. of $H_2SO_4 = \dfrac{13}{100} \times 1000 = 130 g$

moles, $n = \dfrac{130}{98} = 1.326$

Wt. of solvent = 870g

Volume of $sol^n = \dfrac{1}{s} = \dfrac{1000}{1.020} = 980.39 \, cm^3 = 980.39 \, ml$

Molarity $= \dfrac{1326}{980.39} \times 1000 = 1.35 M$

Molality $= \dfrac{n}{W_s} = \dfrac{1.326 \times 1000}{870} = 1.52 m$

**Sol 13:** We have,

$\pi = CRT$

$\therefore C = \dfrac{\pi}{RT} = \dfrac{7.2}{0.0821 \times 310}$

$\left( T = 37^0 C = 310 K \right)$

$C = 0.283 M$

**Sol 14:** $\pi = CRT$

$C = \dfrac{\pi}{RT} = \dfrac{2.45}{0.0821 \times 300} \Rightarrow C = 0.099 M$

**Sol 15:** We have,

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
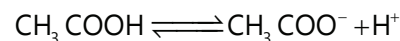
$n = 2$, $\alpha = 0.23$

$i = 1 + (n-1)\alpha = 1 + 0.23 = 1.23$

Now, $n = \dfrac{3 \times 10^{-3}}{60 \times 10^{-3}} = 0.05$

Mass of water = Vs

$= 500 \times 0.997$

$= 498.5 \, gm$

$\therefore m = \dfrac{0.05 \times 1000}{498.5}$

$m = 0.1$

$\therefore \Delta T_f = i \, m \, k_f = 1.23 \times 0.1 \times 1.86$

$\Delta T_f = 0.23 k$

**Sol 16:** Let moles of $Na_2CO_3$ and $NaHCO_3$ be n each and wt. of $NaHCO_3$ be x then,

$\dfrac{x}{84} = \dfrac{1-x}{104} \dfrac{n}{V} \Rightarrow x = 0.446 g$

Then, $n = \dfrac{x}{84} = 5.32 \times 10^{-3}$

Now, moles of HCl = moles of

$NaHCO_3 + 2(moles \, of \, Na_2Co_3)$

$$\Rightarrow \frac{V \times 0.1}{1000} = 5.32 \times 10^{-3}(1+2) = V = 158.9 ml$$

**Sol 17:** we have,

$$M = \frac{k_B w_B}{\Delta T_B \times w_A} \times 1000$$

$$= \frac{2.53 \times 180 \times 1000}{(354.11 - 353.23) \times 90} = M = 57.5 g\ mol^{-1}$$

**Sol 18:** $M = \dfrac{k_f \times w_B}{\Delta T_f \times w_A} \times 1000 = \dfrac{5.12 \times 1}{0.4 \times 50} \times 1000$

$$M = 256 g\ mol^{-1}$$

**Sol: 19:** We have, $P = 0.8P_0$

$$\therefore X_A = \frac{P_0 - P}{P_0} = 0.2$$

$$0.2 = \frac{\dfrac{M}{40}}{\dfrac{M}{40} + \dfrac{114}{114}}$$

$$\Rightarrow \frac{M}{200} + 0.2 = \frac{M}{40}$$

$$\Rightarrow M = 10 g$$

**Sol 20:** $\Delta T_b = k_b m$

But, $k_b = \dfrac{R T_b^2}{1000 \times \Delta H_v}$

$$\therefore T_b = \frac{R T_b^2}{1000 \times \Delta H_v}.m$$

or $\Delta T_b \propto \dfrac{1}{\Delta H_v}$

**Sol 21: (a)** For egg shell placed in pure water, endosmosis will take place and shell will swell.

For Egg shell placed in saturated NaCl solution, exosmosis will occur and shell will shrink.

**(b)** $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$
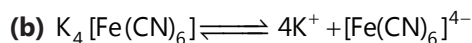
$n = 5$

$\alpha = 0.5$

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

$\Rightarrow 1 + 4\alpha$

$\Rightarrow 3$

$\pi = iCRT$

$= 3 \times 0.1 \times 0.0821 \times 300 = 7.389 atm$

**Sol 22:** For reasons and equations, refer text

$KCl \rightleftharpoons K^+ + Cl^-$
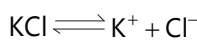
$n = 2$

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

$\therefore \pi = iCRT$

$$i = \frac{\pi}{CRT}$$

$$1 + \alpha = \frac{4.68 \times 74.5}{7.45 \times 0.0821 \times 300}$$

$1 + \alpha = 1.9$

$\alpha = 0.9$

Degree of dissociation = 90%

**Sol 23:** $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
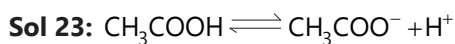
$\qquad\qquad 1-\alpha \qquad\qquad \alpha \qquad\qquad \alpha$

$$k_a = \frac{\alpha^2}{1-\alpha}$$

$n = 2$

$i = 1 + \alpha$

$\Delta T_f = i k_f m$

Weight of acetic acid $= 1.06 \times 0.6 = 0.636 g$

$$m = \frac{0.636}{\dfrac{60}{1}} = 0.0106$$

$$i = \frac{0.0205}{1.86 \times 0.0106} = 1.04$$

$\alpha = 0.04$

$$k_a = \frac{C\alpha^2}{1-\alpha} = \frac{1.06 \times 0.6}{60} \times \frac{(0.04)^2}{(1-0.04)}$$

$$k_a = 18.6 \times 10^{-6}$$

**Sol 24:** We have,

$$M = \frac{k_f \times w_a}{\Delta T_f \times w_s} \times 1000$$

Let atomic mass of A and B be a and b respectively.

$$\therefore a + 2b = \frac{5.1 \times 1}{2.3 \times 20} \times 1000 = 110.87$$

$a + 4b = \dfrac{5.1 \times 1}{1.3 \times 20} \times 1000 = 196.15$
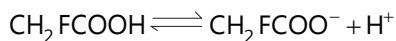
$\therefore 2b = 85.28$

$b = 42.64$

$a = 25.60$

**Sol 25:** $k_f = 1.86$

$[CH_2FCOOH].C = \dfrac{19.5 \times 1000}{78 \times 500} = 0.5M$

$m = \dfrac{\dfrac{19.5}{78}}{\dfrac{500}{1000}} = 0.5m$

$CH_2 FCOOH \rightleftharpoons CH_2 FCOO^- + H^+$

$C - C\alpha \quad C\alpha \quad C\alpha$

$n = 2$

$i = 1 + \alpha$

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

$i = \dfrac{1}{1.86 \times 0.5} = 1.075$

$\alpha = 0.075$

$k_a = \dfrac{C\alpha^2}{1 - \alpha} = 3.06 \times 10^{-3}$

**Sol 26:** $P_T = P_a = P_c = 741.8\,X_a + 632.8\,X_c$

$= 741.8\,X_a + 632.8\,(1 - X_a)$

$P_T = 632.8 + 109\,X_a$

$P_C = 632.8 - 632.8\,X_a$

$P_a = 632.8\,X_a$

Plotting this and given that a
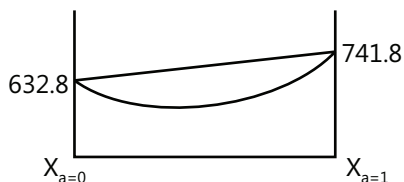


It will show negative deviation

**Sol 27:**

(a) Refer text

(b) (i) $= 1 - \left(1 - \dfrac{1}{n}\right)\alpha$

$1 - \left(1 - \dfrac{1}{2}\right) = \dfrac{1}{2}$

$\dfrac{P_0 - P}{P_0} = iX = \dfrac{1}{2} \cdot \dfrac{\dfrac{61}{122}}{\dfrac{61}{122} + \dfrac{500}{78}}$

$\dfrac{66.6 - P}{66.6} = 0.036$

$P = 64.20\,torr$

(ii) $\dfrac{P_0 - P}{P_0} = 0.072$ ; $P = 61.78\,torr$

(iii) Refer Text

**Sol 28:** (a) For 1 molal

$i = \dfrac{n}{w_s} \approx \dfrac{n}{qV}$

For 1 molar $= 1 = \dfrac{n}{V}$

For density, $p > 1 : 1$ molal will have more concentration.

(b) $KCl \rightleftharpoons K^+ + Cl^-$
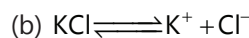
$n = 2$

$i = 1 + \alpha$

$m = \dfrac{\dfrac{0.5}{74.5}}{\dfrac{100}{1000}} = 0.067$

$\Delta T_f = i k_f m$

$i = \dfrac{0.24}{1.86 \times 0.067} = 1.92$

$\Rightarrow \alpha = 0.92$

92% ionisation

**Sol 29:** As, we increase the pressure over a gas, the number of gaseous particles per unit volume increase and also the rate at which the gases are striking the surface of solution to enter it. According to Le-Chatelier's principle, the gas will try to return to its previous state and its solubility will increase, until a new equilibrium is reached resulting in an increase in the pressure of the gas above the solution and hence its solubility increase.

## Exercise 2

**Single Correct Choice Type**

**Sol 1: (C)** We have,

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

$= 0.4 \times 100 + 0.6 \times 200$

$= 40 + 120 = 160$ mm Hg

$P_A = 40\, mmHg$

$P_A = P.Y_A$

$Y_A = \dfrac{40}{160} = 0.25$

**Sol 2: (C)** Raoult's Law $= \dfrac{P_0 - P}{P_0} = \dfrac{n}{n+N}$

$\dfrac{n+N}{n} = \dfrac{P_0}{P_0 - P}$

$1 + \dfrac{N}{n} = \dfrac{P_0}{P_0 - P}$

$\dfrac{N}{n} = \dfrac{P_0 - P_0 + P}{P_0 - P} \Rightarrow \dfrac{P_0 - P}{P} = \dfrac{n}{N}$

**Sol 3: (A)** $P = X_A P_A^0 + X_B P_B^0$

$= \dfrac{1}{1+3}.100 + \dfrac{3}{1+3}.80 = 25 + 60 = 85$ mm Hg

**Sol 4: (A)** $\Delta T_b = i k_b m$

$T_b$ will be highest for solute for which $\Delta T_b$ is highest or i is highest.

For same degree of dissociation, $i \propto n$, n is largest for $Al_2 (SO_4)_3 \, (n = 5)$

**Sol 5: (C)** $\dfrac{P_0 - P}{P_0} = X_a$

$\dfrac{\Delta P}{P_0} = X_a$

$\dfrac{\Delta P_1}{\Delta P_2} = \dfrac{X_{a_1}}{X_{a_2}}$

$\dfrac{10}{20} = \dfrac{0.2}{X_{a_2}} \Rightarrow X_{a_2} = 0.4$

$\therefore X_S = 1 - 0.4 = 0.6$

**Sol 6: (D)** For every 1L solution, moles of glucose = 1, weight of $sol^n = 1.2 \times 1000 = 1.2$ kg

Weight of glucose = 180 g

Weight of solvent = 1200−180=1020g

$\therefore$ molality $= \dfrac{1}{1.02} = 0.98\, m$

$\therefore \Delta T_b = K_b\, m = 0.98 K_b$

**Sol 7: (B)** $i = \dfrac{\text{Normal molecular wt}}{\text{Observed molecular wt}} > 1$

$\Rightarrow$ Observed molecular wt < normal molecular wt.

**Sol 8: (D)** $A_2 B_3 \rightleftharpoons 2A^+ + 3B^-$

$\alpha = 0.6$

n = 5

$i = 1 + (n-1)\alpha = 3.4$

$\Delta T_b = i K_b\, m$

$= 3.4 \times 0.52 \times 1$

$= 1.768 K$

$T_b = 373 + 1.768 = 374.768$ K

**Sol 9: (B)** Since, glucose does not dissociate, $n = 0 \Rightarrow i = 1$

**Sol 10: (B)** $\Delta T_b = i K_b\, m$

For v equimolar solution are equimolal also very dilute.

$\therefore \Delta T_b \propto i$

$i_{AlCl_3} > i_{CaCl_2}$

(as $i \propto n$, $n_{AlCl_3} = 4, n_{CaCl_2} = 2$)

$\Delta T_b\, AlCl_3 > \Delta T_b\, CaCl_2$

$T_1 > T_2$

**Sol 11: (C)** $\Delta T_f = i K_f\, m$

$i = \dfrac{\Delta T_f}{K_f\, m} = = \dfrac{0.0054}{1.86 \times 0.001} = 2.903$

$\alpha = 1$

$\therefore 1 + (n-1)\,\alpha = 2.9 \approx 3$

n − 1 = 2

n = 3

$\therefore$ Out of the given options, only (C) is possible

**Sol 12: (B)** We have

$P = 0.95\, P_0$

$\dfrac{P_0 - P}{P_0} = X_a = 0.05$

$\dfrac{\dfrac{w_a}{M_a}}{\dfrac{w_a}{M_a} + \dfrac{w_b}{M_b}} = 0.05$

$\dfrac{w_a}{M_a} = \dfrac{1}{20}\dfrac{w_a}{M_a} + \dfrac{1}{20}\dfrac{w_b}{M_b}$

$\dfrac{19}{20}\dfrac{w_A}{M_a} = \dfrac{1}{20}\dfrac{w_b}{M_b}$

$\dfrac{w_b}{w_A} = 19 \cdot \dfrac{M_b}{M_a}$

$19 \times 0.3 = 5.7$

**Sol 13: (A)** $XCl_3 \rightarrow X + 3Cl$

$n = 4$

$\alpha = 1$

$i = 1 + 3 = 5$

$X_A = \dfrac{P_0 - P}{P_0}$

$X_A = \dfrac{17.25 - 17.2}{17.25 \times 4}$

$X_A = 7.24 \times 10^{-4} = \dfrac{n}{n + N}$

For $n + N = 1$, $n = 7.24 \times 10^{-4}$

$N = 0.999$

$m_w = \dfrac{N.18}{1000}$

$V_w = \dfrac{N.18}{1000} L$

$\therefore [A] = \dfrac{n}{V_w}$

$\dfrac{X_A . 1000}{(1 - X_A).18}$

$[A] = 4.04 \times 10^{-2}$ mole/L

**Sol 14: (C)** Initially

$P = P_A + P_B = P_A^0 \cdot X_A + P_B^0\, X_B$

$600 = \dfrac{3}{5}P_A^0 + \dfrac{2}{5}P_B^0$

$3P_A^0 + 2P_B^0 = 3000$

$9P_A^0 + 6P_B^0 = 9000$ ... (i)

After adding C,

$P = P_A + P_B$

$630 = \dfrac{3 + 1.5}{3 + 2 + 1.5 + 0.5}P_A{}^0 + \dfrac{2}{3 + 2 + 1.5 + 0.5}P_B{}^0$

$630 = \dfrac{9}{14}P_A{}^0 + \dfrac{4}{14}P_B{}^0$

$9P_A{}^0 + 4P_B{}^0 = 8820$ ... (ii)

(i)- (ii) $\rightarrow 2P_B{}^0 = 180$

$P_B{}^0 = 90\,\text{torr}$

**Sol 15: (B)** $HX \rightleftharpoons H^+ + X^-$

$n = 2$

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

$m = M = 0.1$

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

$i = \dfrac{\Delta T_f}{k_f\, m} = \dfrac{0.2}{1.8 \times 0.1} = 1.11$

$\alpha = 0.11$

$\therefore k_a = \dfrac{C\alpha^2}{1 - \alpha} = \dfrac{0.1 \times (0.11)^2}{(1 - 0.11)} = 1.35 \times 10^{-3}$

**Sol 16: (C)** $P_T$ vs $X_B$ is linear

$P_T = P_A{}^0 \cdot X_A + P_B^0 \cdot X_B$

$P_B = Y_B\, P_T$

$P_B{}^0\, X_B = Y_B\, (P_A{}^0\, X_A{}^0 + P_B{}^0\, X_B{}^0)$

$\Rightarrow \dfrac{1}{P_T} = \dfrac{1}{P_B} \cdot Y_B$ Linear $= \dfrac{1}{P_A}Y_A$

**Sol 17: (D)** $P = P_A^0\, X_A + P_B^0 X_B$

$= \dfrac{100.2}{5} + 300\dfrac{3}{5} = 40 + 90 = 130$ torr

**Sol 18: (B)** $Ba(NO_3)_2 \rightarrow Ba^{2+} + 2NO_3{}^-$

$n = 3$

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

$i = 1 + 2\alpha$

$2.74 = 1 + 2\alpha$

$\alpha = \dfrac{1.74}{2} = 0.87 = 87\%$

## Previous Years' Questions

**Sol 1: (A)** $P_{N_2} = K_H \times X_{N_2}$

$X_{N_2} = \dfrac{1}{10^5} \times 0.8 \times 5 = 4 \times 10^{-5}$

in 10 mole, solubility is $4.0 \times 10^{-4}$

**Sol 2: (D)** Basicity of $H_3PO_3$ is 2.

Hence 0.3 M $H_3PO_3$ = 0.6 N.

**Sol 3: (C)** With increase of temperature, fraction of solute present in water changes.

**Sol 4: (A)** For HCl M = N = 0.1

$N_1V_1 = N_2V_2$; $25 \times N_1 = 0.1 \times 35$

$N_1 = \dfrac{0.1 \times 35}{25}$;

$\therefore M = \dfrac{0.1 \times 35}{25 \times 2} = 0.07$

**Sol 5: (B)** Mobility do not depends on temp. as it do not depends on volume.

**Sol 6: (C)** $M_1V_1 + M_2V_2 = M_3V_3$;

$1.5 \times 480 + 1.2 \times 520 = M \times 1000$

$M = \dfrac{720 + 624}{1000} = 1.344$ M

**Sol 7: (B)** An increase in temperature increases the volume of the solution and thus decreases its molarity.

**Sol 8: (B)** Mole urea $= \dfrac{0.02 \times 10}{6.02 \times 10^{23}} = 10^{-3}$ moles

Conc. of solution (in molarity) $= \dfrac{10^{-3}}{100} \times 1000 = 0.01$ M

**Sol 9: (A)** $H_3PO_3$ is a dibasic acid

$N_1V_1$(acid) = $N_2V_2$(base)

$0.1 \times 2 \times 20 = 0.1 \times 1 \times V_2$

$\therefore V_2 = \dfrac{0.1 \times 2 \times 20}{0.1 \times 1} = 40$ mL

**Sol 10: (C)** $X_{methyl\ alcohol} = \dfrac{5.2}{5.2 + \dfrac{1000}{18}} = 0.086$

**Sol 11: (D)** Molarity $= \dfrac{\text{moles of sulphur}}{\text{volume of sol.}(l)}$

$= \dfrac{120 \times 1.15}{60 \times 1120} \times 1000 = 2.05$ M

**Sol 12: (C)** Equimolar solutions in the same solvent have same boiling and same freezing point.

**Sol 13: (C)** As $P_T = P_x^0 . X_x + P_y^0 . X_y$

$550 = P_x^0 . \dfrac{1}{4} + P_y^0 . \dfrac{3}{4}$

$P_x^0 + 3P_y^0 = 2200$ .... (i)

On adding 1 mole of Y (P) be comes 560 so

$560 = P_x^0 . \dfrac{1}{5} + P_y^0 . \dfrac{4}{5}$

$P_x^0 + 4P_y^0 = 2800$ .... (ii)

From eq. (i) and (ii)

$P_x^0 = 400$ mm Hg

$P_y^0 = 600$ mm Hg

**Sol 14: (C)** $\dfrac{P^0 - P_s}{P^0} = \dfrac{n}{n + N}$

$n = \dfrac{18}{180} = 0.1 N = \dfrac{178.2}{18} = 9.9 = 0.1$ N

$\dfrac{175 - P_0}{17.5} = \dfrac{0.1}{0.1 + 9.9}$; $\dfrac{175 - P_0}{17.5} = \dfrac{1}{100}$

$1750 - 100P_s = 17.5$; $1732.5 = 100p_s$

$P_s = 17.325$ mm Hg

**Sol 15: (A)** Let the vapour pressue of pure ethyl alcohol be P,

According to Raoult's law

$290 = 200 \times 0.4 + P \times 0.6$

$P = \dfrac{290 - 80}{0.6} = 350$ mm Hg

**Sol 16: (B)** In solution showing positive type of deviation, the partial pressure of each component of solution is greater than the vapour pressure as expected according to Raoult's law.

In solution of methanol and benzene, methanol molecules are held together due to hydrogen bonding as shown below,

On adding benzene, the benzene molecules get in between the molecule of methanol thus breaking the hydrogen bonds. As the resulting solution has weak intermolecular attraction, the escaping tendency of alcohol and benzene molecule from the solution increases. Consequently, the vapour pressure of the solution is greater than the vapour pressure as expected from Raoult's law.

**Sol 17: (D)** Solution with the same osmotic pressure are isotonic.

Let the molar mass of the substance be M

$\pi_1 = C_1RT = C_2RT = \pi_2$

So, $C_1 = C_2$

As density of the solutions are same

So, $\dfrac{5.25}{M} = \dfrac{15}{60}$; $M = \dfrac{5.25 \times 60}{1.5} = 210$ g mol$^{-1}$

**Sol 18: (C)** Value of R = 8.314 J mol$^{-1}$ K$^{-1}$

**Sol 19 (A)** During depression of freezing point in a solution liquid solvent, solid solvent are iin equilibrium.

**Sol 20: (A)** $A_xB_y \rightarrow xA^{y+} + yB^{x-}$

1– α xα yα

i = 1 – α + xα + ya

i = 1 + α(x + y – 1)

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

**Sol 21: (D)** $P_T = P_A^\circ X_A + P_B^\circ X_B$

$760 = 520X_A + P_B^\circ(1-X_A) \Rightarrow X_A = 0.5$

Thus, mole % of A = 50 %

**Sol 22: (B)** Vant Hoff's factor (i) for $Na_2SO_4 = 3$

$\therefore \Delta T_f = (i) k_f m_k = 3 \times 1.80 \times \dfrac{0.01}{1} = 0.0558$ K

**Sol 23: (D)** $\Delta T_f = K_f \times m = K_f \times \dfrac{w_2 \times 1000}{w_1 \times m_2}$

$w_1$ and $w_2$ = wt of solvent and solute respecting

$m_2$ = mw of solute

$\Delta T_f = 0^\circ - (-6^\circ) = 6 = 1.86 \times \dfrac{w_2 \times 1000}{w_1 \times m_2}$

Therefore $w_2 = 800$ g

**Sol 24: (B)** $\Delta T_f = K_f.m$

$2.8 = 1.86 \times \dfrac{wt}{62} \times \dfrac{1000}{1000}$

Wt = 93 g

**Sol 25: (A)** $\pi = i$ CRT

$\pi_{C_2H_5OH} = 1 \times 0.500 \times R \times T = 0.5$ RT

$\pi_{Mg_3(PO_4)_2} = 5 \times 0.100 \times R \times T = 0.5$ RT

$\pi_{KBr} = 2 \times 0.250 \times R \times T = 0.5$ RT

$\pi_{Na_3PO_4} = 4 \times 0.125 \times RT = 0.5$ RT

**Sol 26: (B)** $\dfrac{P_0 - P_S}{P_S} = \dfrac{n}{N}$

$\dfrac{185 - 183}{183} = \dfrac{1.2 / M}{100 / 58}$

$M \approx 64$ g / mol

**Sol 27: (B)** Moles of glucose $= \dfrac{18}{180} = 0.1$

Moles of water $= \dfrac{178.2}{18} = 9.9$

$\Rightarrow n_{Total} = 10$

$\Rightarrow \dfrac{\Delta P}{P^\circ} = \dfrac{0.1}{10}$

$\Rightarrow \Delta P = 0.01 P^\circ$

$= 0.01 \times 760 = 7.6$ torr

$P_S = 760 - 7.6 = 752.4$ torr

# JEE Advanced/Boards

## Exercise 1

**Sol 1:** $P_{CH_3OH} = P_A^0 \cdot X_A = 23$

$X_A = \dfrac{23}{96} = 0.24$

**Sol 2:** $\dfrac{P_0 - P}{P_0} = X_B$

$\dfrac{0.8 - 0.6}{0.8} = X_B$

$X_B = 0.25$

**Sol 3:** $X_g = \dfrac{\dfrac{20}{180}}{\dfrac{20}{180} + \dfrac{70}{18}} = 0.027$

$\dfrac{P_0 - P}{P_0} = X_g$

$\dfrac{25.21 - P}{P_0} = 0.027$

P = 24.51 torr

**Sol 4:** $\dfrac{P_0 - P}{P_0} = X_a$

$\dfrac{23.76 - 23.32}{23.76} = \dfrac{\dfrac{5.4}{M}}{\dfrac{5.4}{M} + \dfrac{90}{18}}$

$\Rightarrow \dfrac{\dfrac{5.4}{M}}{\dfrac{5.4}{M} + 5} = 0.018$

$\Rightarrow \dfrac{5.4}{M} = 0.09 + \dfrac{0.0972}{M}$

$\Rightarrow$ M = 57.24 gm

**Sol 5:** $P = 0.75 P_0$

$\dfrac{P_0 - P}{P_0} = \dfrac{n_u}{n_u + n_w}$

$\dfrac{P_0 - P}{P_0} = \dfrac{n_u}{n_w}$

$\dfrac{P_0 - 0.75 P_0}{0.75 P_0} = \dfrac{w \times 18}{60 \times 100}$

$w = \dfrac{60 \times 100}{3 \times 18}$

w = 111.11 gm

$m = \dfrac{\dfrac{111.11}{60}}{\dfrac{100}{1000}}$

m = 18.52 mol

**Sol 6:** $\Delta T_b = K_b m$

$0.284 = \dfrac{2.11 \times 10.6 \times 1000}{M \times 740}$

$m = \dfrac{2.11 \times 10.6 \times 1000}{740 \times 0.284}$

m = 106.42 g

**Sol 7:** $\Delta T_b = K_b M$

$0.130 = \dfrac{0.513 \times 3.24 \times 1000}{M \times 200}$

$l_c = \dfrac{0.513 \times 3.24 \times 1000}{0.13 \times 200}$

$l_c$ = 64 gm

**Sol 8:** $\Delta T_b = K_b M$

$0.513 \times \dfrac{\dfrac{24}{58}}{600 / 1000}$

$\Delta T_b = 0.353^0 C$

$T_b = 99.725 + 0.353$

$\Delta T_b = 100.078^0 C$

**Sol 9:** $\Delta T_b = K_b M$

$\Delta T_f = K_f M$

$\Delta T_f = \dfrac{K_f}{K_b} \cdot \Delta T_b = \dfrac{0.86}{0.513} \times 0.17 = 0.62^\circ C$

$\therefore T_f = -0.62^0 C$

**Sol 10:** $\pi = CRT$

$C = \dfrac{30}{0.0821 \times 298}$

$C = 1.226\,mole/L$

$M \approx C$

$\Delta T_f = K_f M = K_f C = 1.86 \times 1.226$

$\Delta T_f = 2.28^0\,C$

$\therefore\; T_f = -2.28^0\,C$

**Sol 11:** $P_0 = 760\,mm$

$\dfrac{P_0 - P}{P_0} = \dfrac{760 - 750}{760}$

$\dfrac{1}{76} = X_a$

$X_a = 0.013$

For, $n_A + n_S = 1 \Rightarrow n_A = X_a = 0.013$

$n_S = 1 - n_A = 0.987$

$M_S = 17.766\,g$

$\therefore\; m = \dfrac{n_a}{M_s} = \dfrac{0.013 \times 1000}{17.766}$

$m = 0.741\ Molal$

**Sol 12:** Refer to solution 9, Exercise I

**Sol 13:** We have, $\dfrac{P_0 - P}{P_0} = X_a = \dfrac{P_0 - P}{P_0} = \dfrac{n_A}{n_S}$

$\dfrac{640 - 600}{600} = \dfrac{2.175 \times 78}{M.39}$

$M = 65.25\,gm$

**Sol 14:** $m = 0.5 = \dfrac{n_a}{w_s}$

For 1 kg water, $n_a = 0.5$

$n_w = \dfrac{1000}{18}$

$\therefore\; X_a = \dfrac{n_a}{n_a + n_w} = \dfrac{0.5}{0.5 + \dfrac{1000}{18}}$

$X_a = 8.92 \times 10^{-3}$

$\dfrac{P_0 - P}{P_0} = X_a$

$P = P_0(1.X_a) = 17.54 \times 0.99$

$P = 17.38\,mmHg$

**Sol 15:** For A,

$X_b = X_a = \dfrac{1}{2}$

$P_A = X_b P_b^o + X_a P_b^o = \dfrac{160 + 60}{2}$

$P_A = 110\,mmHg$

For B, Lets mass of each be m.

$n_b = \dfrac{m}{78},\; n_a = \dfrac{m}{92}$

$\therefore\; X_b = \dfrac{\dfrac{m}{78}}{\dfrac{m}{78} + \dfrac{m}{92}} = 0.541$

$P_B = X_b P_b{}^0 + (1 - X_b)P_+^o$

$P_B = 114.11\,atm$

$\dfrac{P_A}{P_B} = \dfrac{110}{114.11}$

$\dfrac{P_A}{P_B} = 0.964$

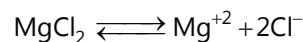**Sol 16:** $\Delta T_b = K_b(i_1 m_1 + i_2 m_2)$

For NaCl

$NaCl \rightleftharpoons Na^+ + Cl^-$
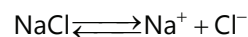
$n = 2,\; \alpha = 0.8$

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

$i = 1 + 0.8$

$i = 1.8$

$m = \dfrac{\dfrac{5.84}{58.5}}{\dfrac{100}{1000}} = 1$

For $MgCl_2$

$MgCl_2 \rightleftharpoons Mg^{+2} + 2Cl^-$
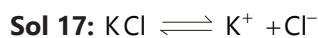
$n = 3,\; \alpha = 0.5$

$i = 1 + 2 \times 0.5 = 2$

$m = \dfrac{\dfrac{9.5}{95}}{\dfrac{100}{1000}} = 1$

$\Delta T_b = 0.51(1.8 \times 1 + 2 \times 1)$

$\Delta T_b = 1.938^0\,C$

$T_b = 101.938^0\,C$

**Sol 17:** $KCl \rightleftharpoons K^+ + Cl^-$

$n = 2, \alpha = 0.95$

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

$i = 1 + 0.95$

$i = 1.95\alpha$

$K_f = \dfrac{RT_f^2}{1000 \times \Delta H_f}$

$\Delta H_f = 80\,cal/gm = 334.72\,J/gm$

$K_f = \dfrac{8.314 \times (273)^2}{1000 \times 334.72} = 1.851$

$M = \dfrac{\dfrac{7.45}{74.5}}{\dfrac{500}{1000}} = 0.2$

$\Delta T_f = iK_f m = 1.95 \times 1.851 \times 0.2 = 0.73°C$

$T_f = -0.73°C$

**Sol 18:** Let n particles be formed after dissociation

Taking $\alpha = 1$

$i = 1 + (n-1) = n$

$\Delta T_f = iK_f .m$

$n = i = \dfrac{0.558}{1.86 \times 0.1} = 3$

Formula $[Co(NH_3)_5 Cl] - Cl_2$

**Sol 19:** Refer Exercise II, Comprehension I

**Sol 20:** At $P_t = 1$

$P_t = P_B^0 X_B + P_T^0 X_T$

$760 = 1375 X_B + 558(1 - X_B)$

$760 = 1375 X_B + 558 - 558 X_B$

$202 = 817 X_B$

$X_B = 0.247$

$X_T = 0.753$

For Vapour

$P_B = Y_B . P_t$

$Y_B = \dfrac{P_B \times B}{P_t} = \dfrac{1375}{760} = 0.447$

**Sol 21:** Pressure must be applied on 0.01 M glucose solution to prevent osmosis.

Excess pressure = $\pi_1 - \pi_2$

$(C_1 - C_2)RT$

$(0.01 - 0.001) \times 0.0821 \times 300 = 0.2217\,atm$

**Sol 22:**

$\pi_b = CRT$

$\dfrac{\pi_1}{\pi_2} = \dfrac{C_1 T_1}{C_2 T_2}$

$C_2 = \dfrac{\pi_2 C_1 T_1}{\pi_1 t_2}$   $(T_1 = 10°C = 283k)$

$\dfrac{C_2}{C_1} = \dfrac{105.3 \times 283}{500 \times 298}$   $(T_2 = 25°C = 298k)$

$\dfrac{C_2}{C_1} = 0.2$

$C_2 = 0.2 C_1$

$V_2 = 5 V_1$

**Sol 23:** $\Delta T_f = i K_f m$

$0.45 = i \times 5.12 \times \dfrac{\dfrac{0.2}{60}}{\dfrac{20}{1000}}$

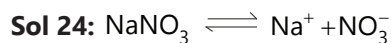$i = 0.527 = 1 - \left(1 - \dfrac{1}{n}\right)\alpha$

$n = 2$

$i = 1 - \dfrac{1}{2}\alpha$

$\alpha = 2(1 - i)$

$\alpha = 0.945$

$\therefore$ 94.51 association

**Sol 24:** $NaNO_3 \rightleftharpoons Na^+ + NO_3^-$

$n = 2, \alpha = 0.9$

$i = 1 + (n-1)\alpha = 1.9$

$\pi = i\,CRT = 1.9 \times \dfrac{0.85}{85} \times 10 \times 0.082 \times 300$

$(T = 27°C = 300k)$

$\pi = 4.64\,atm$

**Sol 25:** $\pi_1 = \pi_2$

$iC_1RT = C_2RT$ (for glucose

$\alpha = 0 \Rightarrow i = 1$)

For NaCl, $i = 1 + (n-1)\alpha = 1 + \alpha$

$(1+\alpha)\dfrac{1.2 \times 10}{58.5} = \dfrac{7.2}{180} \times 10$

$1 + \alpha = 1.95$

$\alpha = 0.95$

$i = 1.95$

**Sol 26:** $2C_6H_5 \rightleftharpoons (C_6H_5COOH)_2$

$n = 2, \alpha = 0.84$

$i = 1 - \left(1 - \dfrac{1}{n}\right)\alpha = i = \dfrac{\alpha}{2} = 0.58$

$\Delta T_b = i K_b M$

$0.58 \times 2.3 \times \dfrac{\dfrac{0.61}{122}}{\dfrac{50}{1000}}$

$\Delta T_b = 0.1334^0\,C$

$T_b = 46.2^0 + 0.1334^0\,C$

$T_b = 46.3334^0\,C$

**Sol 27:** For first distillate

$X_A = X_B = 0.5$

$P_T = \dfrac{P_A^{\,0} + P_B^{\,0}}{2} = \dfrac{100 + 300}{2}$

$P_T = 200\,Torr$

$P_A = X_A P_A^{\,0} = 50\,torr$

$P_A = Y_A P_T$

$Y_A = \dfrac{P_A}{P_T} = \dfrac{50}{200} = 0.25$

$Y_B = 0.75$

For second distillate

$X_A = Y_A = 0.25, X_B = Y_B = 0.75$

$P_T^0 = 100 \times 0.25 + 300 \times 0.75$

$P_T = 250\,Torr$

Now, $P_A = Y_A P_T$

$Y_A = \dfrac{P_A}{P_T} = \dfrac{100 \times 0.25}{250}$

$Y_A = 0.1$

$Y_B = 0.9$

Mole fraction of A in final condensate = 0.1

**Sol 28:** For phenol, n = 2

$i = 1\left(1 - \dfrac{1}{n}\right)\alpha = 1 - \dfrac{\alpha}{2}$

Now,

$\Delta T_f = i R_f m$

$0.69 = \left(1 - \dfrac{\alpha}{2}\right)5.12 \times \dfrac{20}{94} \Rightarrow 1 - \dfrac{\alpha}{2} = 0.63$

$\dfrac{\alpha}{2} = 0.366$

$\alpha = 0.7333$

**Sol 29:**

Mass of $CH_3OH = V \times \rho = 30 \times 0.7980\,gm = 23.94\,gm$

Moles of $CH_3OH, n = 0.748$

mass of water $= 70 \times 0.9984$

$m = \dfrac{n}{m_S^0} = \dfrac{0.748}{69.888} \times 1000$

$m = 10.70$

$\Delta T_f = k_f m = 10.7 \times 1.86$

$\Delta T_f = 19.91^0\,C$

$T_f = -19.91^0\,C$

Mass of final solution $= 23.94 \times 69.888 = 93.828\,gm$

Volume $= \dfrac{Mass}{Density} = \dfrac{93.828}{0.9575} = 98\,ml$

There for Molarity $= \dfrac{n}{V} = \dfrac{0.748}{98} \times 1000 = 7.63\,M$

Molarity = 7.63 M

# Exercise 2

**Single Correct Choice Type**

**Sol 1: (C)** $\because P_A^{\,0} > P_B^{\,0}$

$Y_A$ will be more than $X_A$

i.e $\dfrac{(n_A)L}{(n_B)L} < \dfrac{(n_A)V}{(n_B)V}$

$$\frac{X_A}{X_B} < \frac{Y_A}{Y_B} \Rightarrow \frac{Y_A}{X_A}$$

$$\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$$

**Sol 2: (D)** Relative lowering will be least in $C_{12}H_{22}O_{11}$ which will not dissociate; i = 1

For rest, i > 1 and show greater decrease.

**Sol 3: (C)** $P = P_A + P_B$

$$X_A P_A + X_B P_B^0$$

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

$$P = P_A^0 - X_P (P_A^0 - P_B^0)$$

$$P_A^0 = 120$$

$$P_A^0 - P_B^0 = 75$$

$$P_B^0 = 45$$

**Sol 4: (D)** A liquid mixture having composition corresponding to point z in the figure shown in subjected to distillation at constant pressure, composition of an azeotrope alters on changing the external pressure

**Sol 5: (B)** From the graph

When $X_{Benzene}$ = 0.5 $Y_{Toluene}$ = 0.8

When $Y_{Toluene}$ = 0.3 $Y_{Benzene}$ = 0.6

$X_{Benzene}$ = 0.3, $Y_{Toluene}$ = 0.9

$X_{Benzene}$ = 0.7, $Y_{Toluene}$ > 0.3

**Sol 6: (C)** $\Delta H_{mix}$ = 0

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -T\Delta S$$



ΔG=-TΔS

TΔS

ΔG

O

X
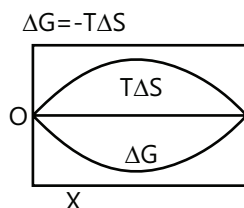
**Sol 7: (D)** Through a semipermeable membrane, only solvent can flow and not the solute.

**Multiple Correct Choice Type**

**Sol 8: (A, C, D)** Only (B) is wrong.

**Sol 9: (A, D)** For ideal solution.

$$\Delta H = 0, \Delta V = 0$$

**Sol 10: (A, C)** Both are correct facts.

**Sol 11: (A, B, C)** All are correct.

**Sol 12: (A, C, D)** Degree of dissociation increases as c decrease

$$\left( \alpha = \sqrt{\frac{R_a}{c}} \right)$$

For ideal soln., $\Delta G = \Delta H - T\Delta S$

$$\Delta G = -T\Delta S \ (H = 0)$$

$$\Delta S = \frac{-\Delta G}{T} > 0 \ (\because \Delta G < 0)$$

**Sol 13: (A, B, C)** Due to polarity and H-bonding.

**Sol 14: (A, D)** For ideal solution.

$$\Delta H = 0, \Delta V = 0$$

**Sol 15: (A, B)** $P_M = X_A P_A^0 + X_B P_B^0$

$$P_M = X_A P_A^0 + P_B^0 - X_A P_B^0$$

$$\frac{P_M - P_B^0}{P_A^0 - P_B^0} = X_A$$

$$P_A = P_T X_{A(V)}$$

$$X'_{A(V)} = \frac{P_A}{P_T} = \frac{X_{A(\ell)} \cdot P_A^0}{P_T}$$

$$\frac{X_{A(\ell)}}{X^1_{A(V)}} = \frac{P_T}{P_A^0}$$

**Sol 16: (A, C, D)** $K_3 PO_4 \rightarrow 3K^+ + PO_4^{3-}$

n = 4

$$i = 1 + (n-1) \alpha = 1 + 3\alpha$$

$$\frac{\Delta P}{P^0} = i X_A$$

$m = \dfrac{n}{w_s}$

For 1 kg solved, $N = \dfrac{1000}{18}$

$m = \dfrac{18n}{1000}$

$n = \dfrac{1000m}{18}$

$X = \dfrac{n}{n+N} = \dfrac{1000m}{18\left(\dfrac{1000m}{18} + \dfrac{1000}{18}\right)}$

$X = \dfrac{m}{m+1}$

$\dfrac{\Delta P}{P^0} = \dfrac{in}{N+n} \approx \dfrac{in}{N}$

$\dfrac{\Delta P}{P^0} = \dfrac{(1+3\alpha)m \cdot 18}{1000}$

$\dfrac{\Delta P}{P^0} = \dfrac{\Delta T_f}{K_f} \cdot \dfrac{18}{1000}$

$1 + 3\alpha = \dfrac{M_w}{M_{w\,obs}}$

**Sol 17: (B, D)** Vant-hoff factor for a dil. sol. of $BaCl_2$ is $1 + 3 - 1 = 3$ (D) is correct

$\Delta T_b$ is also due to lowering in vapour pressure.

**Sol 18: (B, D)** Acetone and ethanol will show negative deviation due to H-bonding between them.

Chloroform and benzene will show positive deviation because of intramolecular H-bonding in chloroform.

**Assertion Reasoning Type**

**Sol 19: (C)** The added substance once must be non - volatile.

**Sol 20: (D)** As heat must be removed from the water to make it freeze, it is exothermic process.

**Comprehension Type**

**Sol 21: (A)** $\Delta T_f = i\,k_f\,m$

$\Delta T_f \propto i$

And $i \propto n$

$n$ is maximum for $Al_2(SO_4)_3$

**Sol 22: (B)** Correction factor is 1

**Sol 23: (B)** $Ba(NO_3)_2 \rightleftharpoons Ba^{2+} + 2NO_3^{-}$

$n = 3$

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

$\alpha = \dfrac{i-1}{n-1} = \dfrac{2.74-1}{3-1}$

$\alpha = 0.87$

8.7% dissociation

**Sol 24: (C)** Colligative effects involve properties whose magnitude depends upon number of particles.

**Sol 25: (B)** $\dfrac{\Delta T_b}{\Delta T_f} = \dfrac{k_b}{k_f}$

$\Delta T_f = \dfrac{0.186 \times 0.521}{1.86} = 0.0521$

**Sol 26:** A → p, r

This mixture will be show positive deviation due to H-bonding between $C_2H_5OH$ and $H_2O$

B → q, t

They will form ideal solution as

$F_{A-A} = F_{A-B} = F_{B-B}$

No strong interactions

C → q, t

This is Raoult's law for ideal solution

D → p, s

Very strong intramolecular H-bonding in $H_2SO_4$ leads to negative deviation.

**Sol 27:** A → r

No dissociation in any of these

$\therefore i = 1$ for all.

B → s

Strong electrolytes, $\alpha = 1$

$1+(2-1): 1+(3-1): 1+(3-1) = 2:3:3$

C → p

$1+(5-1):1+(4-1):1+(5-1) = 5:4:5 = 1:0.8:1$

D → q

$1:1+(2-1):1+(3-1)$

1:2:3

**Sol 28:** A → s

Definition of ppm

B → r

C→ q

D→ p

# Previous Years' Questions

**Sol 1: (C)** In case of positive deviation from Raoult's law, the observed vapour pressure is greater than the ideal vapour pressure and boiling of azeotrope becomes lower than either of pure liquid.

**Sol 2: (A)** $K_2SO_4$: i = 3; NaCl: i = 2

Urea i = 1; Glucose: i = 1

Greater the value of 'i', greater the lowering in freezing point, lower will be the freezing temperature, if molarity, in all cases are same. Therefore, $K_2SO_4$ solution has the lowest freezing point.

**Sol 3: (A)** During freezing, liquid solvent solidify and solid solvent remains in equilibrium with liquid solvent.

**Sol 4: (A)** Van't Hoff factor (i) = 4 $\{3K^+ + [Fe(CN)_6]\}^{3-}$

Molality = $\frac{0.1}{329} \times \frac{1000}{100} = \frac{1}{329}$ ⟹ $-\Delta T_f = iK_f m$

$= 4 \times 1.86 \times \frac{1}{329} = 2.3 \times 10^{-2}$

⟹ $T_f = -2.3 \times 10^{-2}$ °C

(As % freezing point of water is 0°C)

**Sol 5: (D)** In the given solution 'M', $H_2O$ is solute

Therefore, molality of $H_2O$

$= \frac{0.1}{0.9 \times 46} \times 1000 = 2.4$

⟹ $-\Delta T_f = k_f^{ethanol} \times 2.4 = 2 \times 2.4 = 4.8$

⟹ Tf = 155.7 −4.8= 150.9 K

**Sol 6: (A)** Vapour pressure = p($H_2O$) + p(ethanol)

= 32.8 × 0.1 + 40 × 0.9

= 3.28 + 36 = 39.28 mm

**Sol 7: (B)** New ethanol is solute.

Molality of solute = $\frac{0.1}{0.9 \times 18} \times 1000 = 6.17$

⟹ $\Delta T_b$ = 6.17 × 0.52 = 3.20

⟹ $T_b$ = 373 +3.2 = 376.2 K

**Sol 8:** $\lim_{m \to 0}\left(\frac{\Delta T_f}{m}\right) = k_f$ (Cryoscopic constant)

**Sol 9:** From lowering of vapour pressure information:
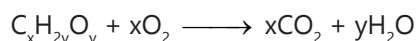
$\frac{0.104}{17.5} = x_2 = \frac{n_2}{n_1 + n_2}$

⟹ $\frac{n_1}{n_2}$ + 1 = 168.27

⟹ $\frac{n_1}{n_2}$ = 167.27

⟹ $\frac{1000}{18} \times \frac{M}{50}$ = 167.27

⟹ M = 150g/mol

Also, the combustion reaction is:

$C_xH_{2y}O_y + xO_2 \longrightarrow xCO_2 + yH_2O$

∴ 18y g of $H_2O$ is produced from 1.0 mole of compound.

∴ 0.9 g of $H_2O$ will be produced from $\frac{0.9}{18y} = \frac{1}{20y}$ mol

⟹ At the end, moles of $O_2$ left = $\frac{x}{20y}$

Moles of $CO_2$ formed = $\frac{x}{20y}$

⟹ Total moles of gases at STP = $\frac{2x}{20y} = \frac{2.24}{22.4}$

⟹ x = y

⟹ Molar mass; 150 = 12x + 2x + 16x = 30x

⟹ x = $\frac{150}{30}$ = 5

⟹ Formula = $C_5H_{10}O_5$

**Sol 10:** Moles of ethanol = $\frac{60}{46}$ = 1.3

Moles of methanol = $\frac{40}{32}$ = 1.25

Mole fraction of ethanol = $\dfrac{1.3}{1.3+1.25}$ = 0.51

Vapour pressure of solution = $p_{ethanol}$ + $p_{methanol}$

= 0.51 × 44.5 + 0.49 × 88.7 = 66.16 mm

Mole fraction of methanol in vapour phase

= $\dfrac{p_{methanol}}{\text{Total vapour pressure}} = \dfrac{43.463}{66.16} = 0.657$

**Sol 11:** According to Raoult's law:

$p = p_0 x_1$

$\Rightarrow 600 = 640 \left(\dfrac{n_1}{n_1 + n_2}\right)$

$\Rightarrow \dfrac{n_2}{n_1} = \dfrac{64}{60} - 1 = \dfrac{1}{15}$

$\Rightarrow n_2 = \dfrac{39}{78} \times \dfrac{1}{15} = 0.033$

$\Rightarrow \dfrac{2.175}{M} = 0.033 \Rightarrow M = 65.25$

**Sol 12:** $Ca(NO_3)_2 \longrightarrow Ca^{2+} + 2NO_3^-$

$1 - \alpha \qquad\qquad \alpha \quad 2a$

$i = 1 + 2\alpha$, where, $\alpha = 0.7$

$\Rightarrow i = 1 + 2 \times 0.7 = 2.4$

$\Rightarrow$ Mole fraction of solvent = $\dfrac{n_1}{n_1 + in_2}$

$= \dfrac{\left(\dfrac{100}{18}\right)}{\left(\dfrac{100}{18}\right) + 2.4 \times \dfrac{7}{164}} = 0.982$

$\Rightarrow p = p_0 x_1$

= 760 × 0.982 (VP of $H_2O$ at 100°C = 760 mm of Hg)

= 746.32 mm

**Sol 13:** (i) Empirical formula determination

| Element | C | H | N | O |
|---|---|---|---|---|
| Weight % | 42.86 | 2.40 | 16.67 | 38.07 |
| Moles | 3.57 | 2.40 | 1.19 | 2.38 |
| Simplest ratio | 3 | 2 | 1 | 2 |

$\Rightarrow$ Empirical formula = $C_3H_2NO_2$

(ii) $\Delta T_b = 1.84 = 2.53 \times \dfrac{5.5}{M} \times \dfrac{1000}{45}$

$\Rightarrow M = 168$

Empirical formula weight (84) is half of molar mass, molecular formula is $C_6H_4N_2O_4$ – a dinitro benzene.



$(C_6H_4N_2O_4)$
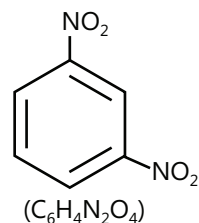
**Sol 14:** Let after 100 min, x moles of A are remaining unpolymerized moles of B = 12.

Mole of non–volatile solute = 0.525

Mole fraction of A = $\dfrac{x}{x+12+0.525}$

Mole fraction of B = $\dfrac{12}{x+12+0.525}$

$400 = \left(\dfrac{x}{x+12+0.525}\right) \times 300 + \left(\dfrac{12}{x+12+0.525}\right) \times 500$

x = 9.9

Moles of A polymerized in 100 min = 10 – 9.9 = 0.10

$k = \dfrac{1}{t} \ln \dfrac{10}{9.9} = \dfrac{1}{100} \ln \dfrac{10}{9.9}$ min⁻1 = 1.005 × 10⁻⁴ min⁻¹.

**Sol 15:** Higher the value of $k_b$ of a solvent suggest that there is larger polarity of solvent molecules, which in turn implies higher boiling point due to dipole–dipole interaction.

Therefore, the correct order of $k_b$ values of the three given solvents is:

| Solvents | Boiling point | $k_b$ |
|---|---|---|
| X | 100°C | 0.63 |
| Y | 27°C | 0.53 |
| Z | 283°C | 0.92 |

**Sol 16: (A)**

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

$2 = 1.72 \times \dfrac{20}{172} \times \dfrac{1000}{50} \times i$

$i = 0.5$

Hence (A) is correct.

**Sol 17: (D)** $\Delta T_f = K_f \times m$

$2 \times \dfrac{0.1}{0.9 \times 46} \times 1000 = 4.83K$

Freezing point of solution M = 155.7 − 4.83 = 150.87 K ≈ 150.9 K

**Sol 18: (B)** P = 0.9 × 40 = 36 mm Hg

**Sol 19: (B)** $\Delta T_b = K_b \times m = 0.52 \times \dfrac{0.1}{0.9 \times 18} \times 1000 = 3.2$ K

Tb = 373 + 3.2 = 376.2 K

**Sol 20: (A)** $P = K_H X_{N_2}$
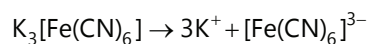
$0.8 \times 5 = 1 \times 10^5 \times X_{N_2}$

$X_{N_2} = 4 \times 10^{-5}$ (in 10 moles of water)

$\Rightarrow 4 \times 10^{-5} = \dfrac{n_{N_2}}{n_{N_2} + 10}$

$n_{N_2} \times 5 \times 10^{-5} + 4 \times 10^{-4} = n_{N_2}$

$\Rightarrow n_{N_2} = 4 \times 10^{-4}$

**Sol 21: (A)**

$K_3[Fe(CN)_6] \rightarrow 3K^+ + [Fe(CN)_6]^{3-}$
$i = 4$

$\Delta T_f = K_f \times i \times \dfrac{m}{M} \times \dfrac{1000}{W} = 1.86 \times 4 \times \dfrac{0.1}{329} \times \dfrac{1000}{100} = 2.3 \times 10^{-2}$

$T_f = -2.3 \times 10^{-2}$

**Sol 22: (A)**

$\Delta T_b = 2°C; \qquad m_a = 2.5g$

$m_{solvent} = 100g \quad K_b = 0.76 K kg mol^{-1}$

$P_{solution} = ?$

$\Delta T_b = K_b \times m$

$2 = 0.76 \times m \qquad\qquad \therefore m = \dfrac{2}{0.76}$

$\dfrac{P^0 - P}{P} = m \times MM \times 10^{-3} \quad \therefore \dfrac{760 - P}{P} = \dfrac{2}{0.76} \times 18 \times 10^{-3}$

$760 - P = \dfrac{36}{760} P \qquad \therefore 760 = \dfrac{796}{760} P$

$\therefore P = 760 \left( \dfrac{796}{760} \right) torr = 725.6 \ torr \approx 724 \ torr$

**Sol 23:**

$\Delta T_f = i \times K_f \times m$
$0.0558 = i \times 1.86 \times 0.01$
$i = 3$

∴ Complex is $[Co(NH_3)_5Cl]Cl_2$

**Sol 24:** $\dfrac{X_{solute}}{X_{solvent}} = \dfrac{0.1}{0.9} = \dfrac{1}{9}$

$\dfrac{W_{solute}}{W_{solvent}} = \dfrac{M_{solvent}}{M_{solute}} = \dfrac{1}{9}$ ... (i)

$W_{solute} + W_{solvent} = W_{solution}$ = density × volume

$W_{solute} + W_{solvent} = 2 \times V$ ... (ii)

Molarity = molality

$\dfrac{n_{solute}}{V_{solvent}} = \dfrac{n_{solute}}{W_{solvent}}$

$W_{solvent} = V_{solution} = \dfrac{W_{solute} + W_{solvent}}{2}$

$\Rightarrow 2W_{solvent} = W_{solute} + W_{solvent}$

$\Rightarrow W_{solute} = W_{solvent}$ ... (iii)

Using eq. (i) and (iii), we get

$\dfrac{M_{solute}}{M_{solvent}} = 9$

**Sol 25: (A, B)** Conceptual fact