

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 liquid	Salt or glucose or sugar or urea solution in water
5.	Liquid	Liquid	Liquid in liquid	Methanol or ethanol in water
6.	Gas	Liquid	Gas in liquid	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 = $\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$

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

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

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

5. Strength of concentration:

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

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

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

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

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

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

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

Molarity \times Number of liters of solution = Number of mole of solute

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

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

MASTERJEE CONCEPTS

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

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

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

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

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

Relation between normality and strength

Normality \times Equivalent mass = $\frac{W_B}{V}$ = Strength of the solution in g/L

Relation between normality and molarity

Normality = $n \times$ 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:

$N_1 V_1 + N_2 V_2 = N_3 (V_1 + V_2)$ or $N_3 = (N_1 V_1 + N_2 V_2) / (V_1 + V_2)$

Similarly, if molarities are used, then $M_3 = (M_1 V_1 + M_2 V_2) / (V_1 + V_2)$

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

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

Illustration 2: The density of a 3M sodium thiosulphate solution ($\text{Na}_2\text{S}_2\text{O}_3$) 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 $\text{S}_2\text{O}_3^{2-}$ 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.

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

No. of moles of $\text{Na}_2\text{S}_2\text{O}_3 = \frac{474}{158} = 3$; mass of water = $(1250 - 474) = 776\text{g}$

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

$$\text{Mole fraction of Na}_2\text{S}_2\text{O}_3 = \frac{3}{43.1 + 3} = \frac{3}{46.1} = 0.065$$

$$\text{No. of moles of Na}^+ \text{ ion} = 2 \times \text{No. of moles of Na}_2\text{S}_2\text{O}_3 = 2 \times 3 = 6$$

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

$$\text{No. of moles of S}_2\text{O}_3^{2-} \text{ ions} = \text{No. of moles of Na}_2\text{S}_2\text{O}_3$$

$$\text{Molality of S}_2\text{O}_3^{2-} \text{ ions} = \frac{3}{776} \times 1000 = 3.86 \text{ m}$$

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.



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

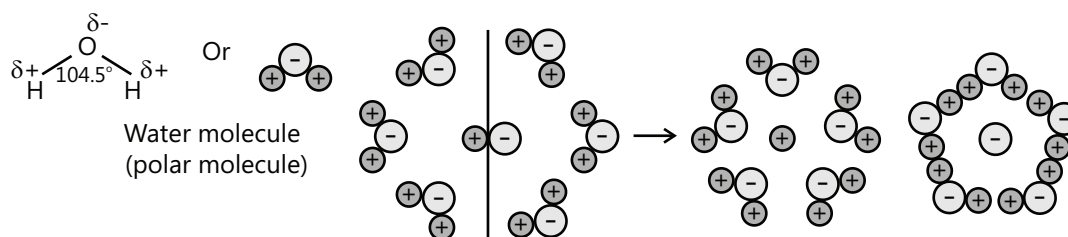


Figure 20.1: Dissociation of an ionic compound, like Na^+Cl^- , in a polar solvent (H_2O)

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., $\Delta_{\text{hyd}} H > \Delta_{\text{lattice}} H$.

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.

MASTERJEE CONCEPTS

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

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

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

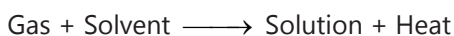
Rohit Kumar (JEE 2012, AIR 79)

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 represented by α .

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



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.

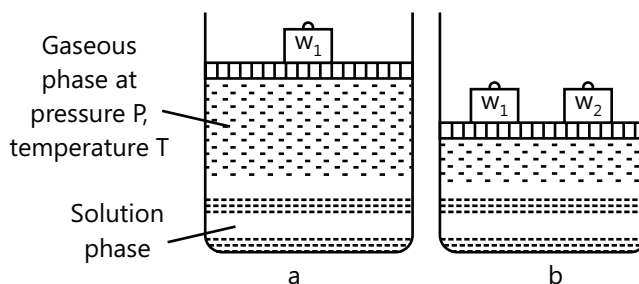


Figure 20.2: Demonstrating the effect of pressure on solubility of a gas in liquid

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.

$$m \propto P \text{ or } m = K_P P$$

In this regard, Dalton also concluded independently that, if a mixture of gases is simultaneously 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 $X_A = K'_P P_A$

However, this can also be written as: $P_A = \frac{1}{K'} X_A$ or $P_A = K_H X_A$ where, $K_H = \frac{1}{K'}$ 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.

MASTERJEE 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 $\frac{m_1}{m_2} = \frac{P_1}{P_2}$.

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.

Aishwarya Karnawat (JEE 2012, AIR 839)

3.3 Solutions of Liquids in Liquids

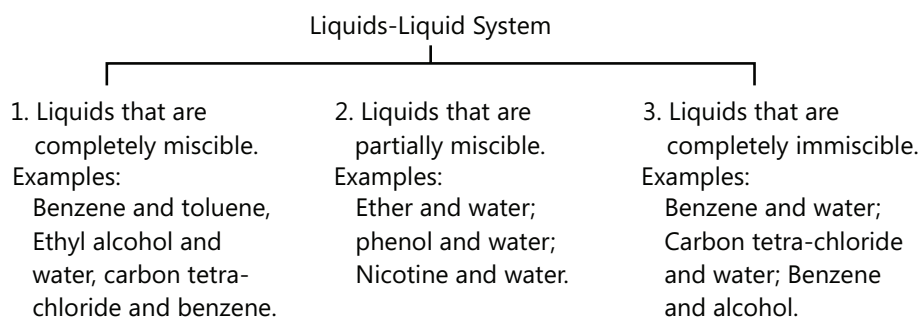
Consider the case wherein one liquid dissolves in another. Here, the molecules of the solvent are forced to move apart so as to accommodate the solute molecules. In the same way, the molecules in the solute must also be separated so that they can assume their positions in the mixture. However, it is 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.



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., $\Delta V_{\text{mix}} = 0$; $V_{\text{Solvent}} + V_{\text{solute}} = V_{\text{solution}}$
- (b) Heat change on mixing should be zero, i.e., $\Delta H_{\text{mix}} = 0$ (heat is neither absorbed nor evolved)
- (c) Solute must not undergo association or dissociation 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) $\Delta H_{\text{mix}} \neq 0$ and
- (c) $\Delta V_{\text{mix}} \neq 0$

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,

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

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

If the total pressure be P , then

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

MASTERJEE CONCEPTS

This law is an important governing factor in deciding whether a solution is ideal or nonideal. Solutions obeying Raoult's law over a wide range of concentrations are ideal; otherwise, they are nonideal.

A non-ideal solution can either show positive or negative deviation from Raoult's law.

Nikhil Khandelwal (JEE 2009, AIR 94)

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 2. $\Delta H_{\text{mix}} = 0$; neither heat is evolved nor absorbed during dissolution 3. $\Delta V_{\text{mix}} = 0$; total volume of solution is equal to sum of volumes of the components 4. $P = P_A + P_B = P_A^0 X_A + P_B^0 X_B$ i.e., $P_A = P_A^0 X_A$; $P_B = P_B^0 X_B$ 5. A – A, A – B, B – B interactions should be same, i.e., 'A' and 'B' are identical in shape, size and character 6. Escaping tendency of 'A' and 'B' should be the same in pure liquid and in the solution Examples Dilute solutions; benzene + toluene	Do not obey Raoult's law $\Delta H_{\text{mix}} > 0$; endothermic dissolution; heat is absorbed $\Delta V_{\text{mix}} > 0$; volume is increased after dissolution $P_A > P_A^0 X_A$; $P_B > P_B^0 X_B$ $\therefore P_A + P_B > P_A^0 X_A + P_B^0 X_B$ 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' and 'B' escape easily showing higher vapor pressure than the expected value Examples Acetone + ethanol; acetone + CS_2	Do not obey Raoult's law $\Delta H_{\text{mix}} < 0$; exothermic dissolution; heat is evolved $\Delta V_{\text{mix}} < 0$; volume is decreased during dissolution $P_A < P_A^0 X_A$; $P_B < P_B^0 X_B$ $\therefore P_A + P_B < P_A^0 X_A + P_B^0 X_B$ A – B attractive force should be greater than A – A and B – B attractive forces. 'A' and 'B' have different shape, size and character. Escaping tendency of both components 'A' and 'B' is lowered showing lower vapor pressure than expected ideally 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 .

$$P_A = Y_A P \quad \dots(\text{i})$$

$$P_B = Y_B P \quad \dots(\text{ii})$$

$$P_A = X_A P_A^0 \quad \dots(\text{iii})$$

$$P_B = X_B P_B^0 \quad \dots(\text{iv})$$

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 pressure of the solution and the mole fraction of methanol in the vapor. **(JEE ADVANCED)**

Sol: Total vapour pressure is a sum of partial pressures 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 then 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 = $X_A \cdot P_A^0 = 0.5107 \times 44.5 = 22.73$ mm Hg

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

Total vapour pressure of solution = $22.73 + 43.40 = 66.13$ 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

- 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 .
- 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.
- 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.
- Thus, we can separate two liquids that form an ideal solution by fractional distillation.

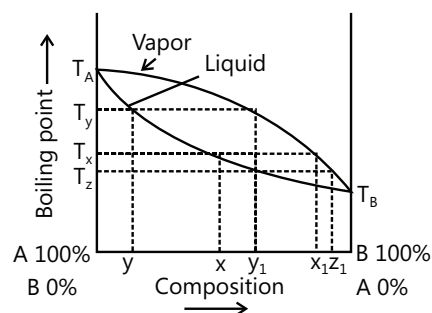


Figure 20.3 a: Composition of solution showing ideal behavior

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

If a mixture of composition x is heated, then

- 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
- 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.
- However, pure B cannot be obtained.

If a mixture of composition y is heated, then

- Vapor will have composition y_1 and residual liquid composition will shift toward C.
- Ultimately, mixture of composition C is obtained as a distillate and pure liquid B is obtained as a residue
- However, it is not possible to obtain pure liquid A.

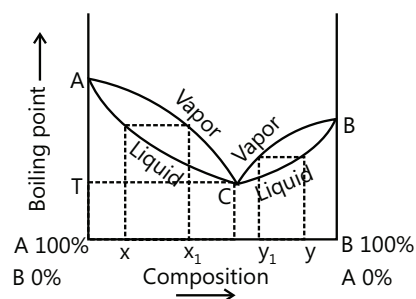


Figure 20.3 b: Composition of solution showing positive deviation from Raoult's law

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

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

- 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.

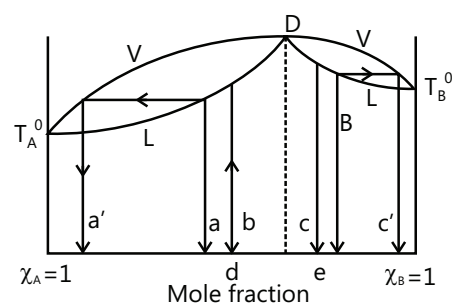


Figure 20.3 c: Mole fraction of solution showing negative deviation from Raoult's law

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.

MASTERJEE 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)

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 $\propto \frac{1}{\sqrt{\text{density}}}$

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

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

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

Substituting the value of χ_A

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

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

\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.

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

or we can rephrase it as ,

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

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.

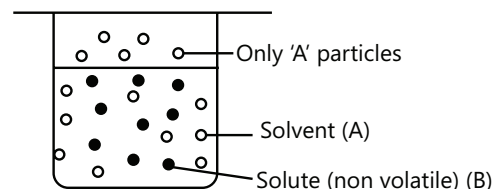


Figure 20.4: Lowering in the Vapor Pressure

MASTERJEE 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, $\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_B + n_A}$.

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

$$\text{we have } n_B = \frac{W_B}{M_A} \text{ and } n_A = \frac{W_A}{M_A}.$$

By substituting these values in the above expression, we obtain

$$\frac{P^0 - P_s}{P^0} = \frac{W_B / M_B}{W_A / M_A + W_B / M_B} \quad \dots (i)$$

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

$$\frac{P^0 - P_s}{P^0} \equiv \frac{n_B}{n_A} \quad \text{or} \quad \frac{P^0 - P_s}{P^0} \equiv \frac{W_B / M_B}{W_A / M_A} \quad \text{or} \quad \frac{P^0 - P_s}{P^0} = \frac{W_B \times M_A}{W_A \times M_B}$$

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^0) 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.

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

$$\Rightarrow \frac{P_0 - P_s}{P_0} = \frac{w_2}{w_1 + w_2} = \frac{\text{Loss in weight of solvent bulbs}}{\text{Total loss in weight of solution bulbs and solvent bulbs}} = X_b$$

i.e., mole fraction of the solute.

Vapor Pressure of Liquid and Temperature



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

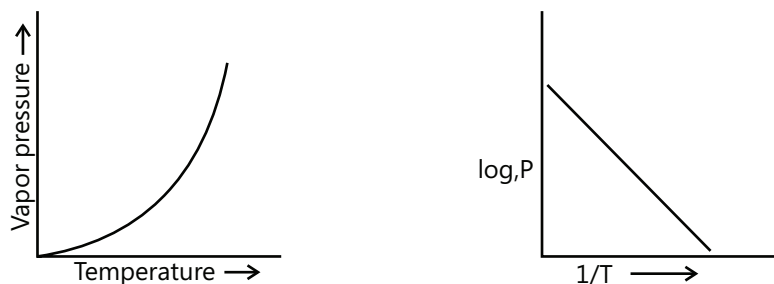


Figure 20.5: Variation of vapor pressure with temperature

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

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

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 addition 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, $(\Delta T) = \text{Boiling point of the solution} - \text{Boiling point of pure solvent}$

This can be better understood by plotting 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.

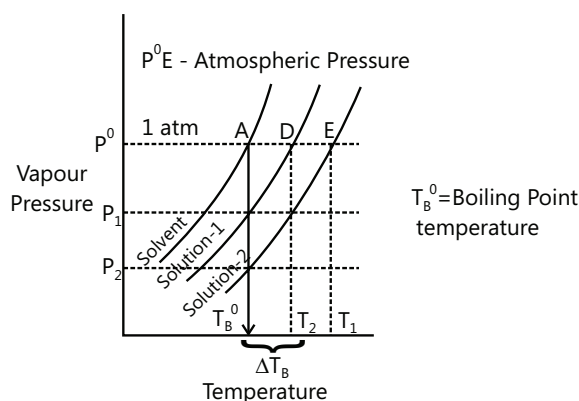


Figure 20.6: Elevation in Boiling Point

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 $\frac{W_B}{M_B} = 1$ mole and W_A = mass of solvent in kilogram (kg)

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

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

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.

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

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

MASTERJEE CONCEPTS

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

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

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

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

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

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

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

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

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 (ΔT) = Freezing point of the solvent – Freezing point of the solution

Here again,

$$\Delta T_f \propto \Delta P$$

$$\Delta P \propto \text{molality} \quad \text{or} \quad \Delta P \propto X_B$$

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

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

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

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

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

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

Hence, molecular weight of solute

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

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 membrane, 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 separated 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

$$V \propto \frac{1}{\pi} \quad (\text{Boyle-van't Hoff law}); \quad V \propto T \quad (\text{Charles-van't Hoff law})$$

$$V \propto n \quad (\text{Avogadro-van't Hoff law})$$

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

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

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

MASTERJEE CONCEPTS

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

where π = 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 $S = 0.08211 \text{ atm deg}^{-1} \text{ mole}^{-1}$

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

where 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., $\frac{n_1}{V_1} = \frac{n_2}{V_2}$; $\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$

- If a number of solutes is present in the solutions and π_1, π_2, π_3 , etc. are their individual osmotic pressure, then the total osmotic pressure = $\pi_1 + \pi_2 + \pi_3 + \dots$

T P Varun (JEE 2012, AIR 64)

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 solutions 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 calculate the molality of the solution.

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

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

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

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

$$\Delta T_b = T_b - T_b^\circ = K_b \cdot m = 3.63 \times 1.50 = 5.44 \text{ K} = 5.445^\circ\text{C}$$

$$T_b = 5.445^\circ\text{C} + T_b^\circ = 5.445^\circ\text{C} + 61.2^\circ\text{C} = 66.645^\circ\text{C}$$

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^3 . 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 = $h \text{ cm}$

$$V = (h \times 1) \text{ cm}^3 \quad \because \text{cross-sectional area} = 1 \text{ cm}^2$$

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

$$\pi = h \times d \times g; \frac{134.92}{h} = \frac{h \times 1}{100} \times \frac{9.8}{101.325}, \quad 1 \text{ atm} = 101.325 \text{ KPa}$$

$$h = 375 \text{ cm} = 3.75 \text{ m}$$

$$\pi = h \times d \times g = 3.75 \times 1 \times 9.8 = 36.7 \text{ KPa}$$

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

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

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

We know that,

$$K_b = \frac{\Delta T_b \times W \times m}{1000 \times w}; \text{ for } \text{CCl}_4, K_b = \frac{0.201 \times 50 \times 128}{1000 \times 0.2563} = 5.019$$

$$K_b \text{ is now used in the second part of the problem; } m = \frac{1000 \times 5.019 \times 0.6216}{0.647 \times 50} = 96.44$$

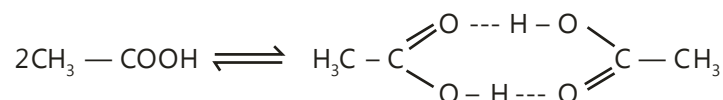
Illustration 10: In a cold climate, water is frozen causing damage to radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at -6°C (K_f for water = $1.85 \text{ K kg mol}^{-1}$). **(JEE ADVANCED)**

Sol: Here we are provided with the value of ΔT , W , m and K_f so we can calculate the weight by using the following formula:

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

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).



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 $37.25 \text{ g} = 74.5/2$. $\text{KCl} \rightleftharpoons \text{K}^+ + \text{Cl}^-$

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, $i = \frac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}}$

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,

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

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.

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

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

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

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

$$\Delta T_B = i K_b m; \Delta T_B = i K_b \times \frac{W_B}{M_B \times W_A (\text{gms})} \times 1000$$

Depression in Freezing Point

$$\Delta T_f = i K_f m; \Delta T_f = i K_f \times \frac{W_B}{M_B \times W_A (\text{gms})} \times 1000$$

Osmotic pressure

$$\pi V = i n R T; \pi = i C R T$$

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

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

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

as $x A^{y+}$ & $y B^{x-}$. ' α ' be degree of dissociation.

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



Initial conc. C 0 0

Conc. at equilibrium $C - C\alpha$ $x C\alpha$ $y C\alpha$

$$i = \frac{[(C - C\alpha) + x C\alpha + y C\alpha]}{C} \Rightarrow i = \frac{1 - \alpha + x\alpha + y\alpha}{1} = 1 + [(x + y) - 1] \alpha$$

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

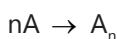
$$\Rightarrow i = 1 + (n - 1) \alpha; \alpha = \frac{i - 1}{n - 1}$$

(b) Association

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

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

Let n molecules of an electrolyte A undergo association



Let the initial concentration of A = C; the degree of association = α

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

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

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

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

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

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

\therefore 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: $3A \rightarrow A_3$

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

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

Total moles present after dissociation

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

$\Delta T_f = K_f m$ or $T_f^0 - T_f = 5.12 \text{ km}^{-1} \times 0.177 m = 0.6$

$T_f = T_f^0 - 0.6^\circ\text{C} = 5.5^\circ\text{C} - 0.6^\circ\text{C} = 4.9^\circ\text{C}$

PROBLEM-SOLVING TACTICS

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

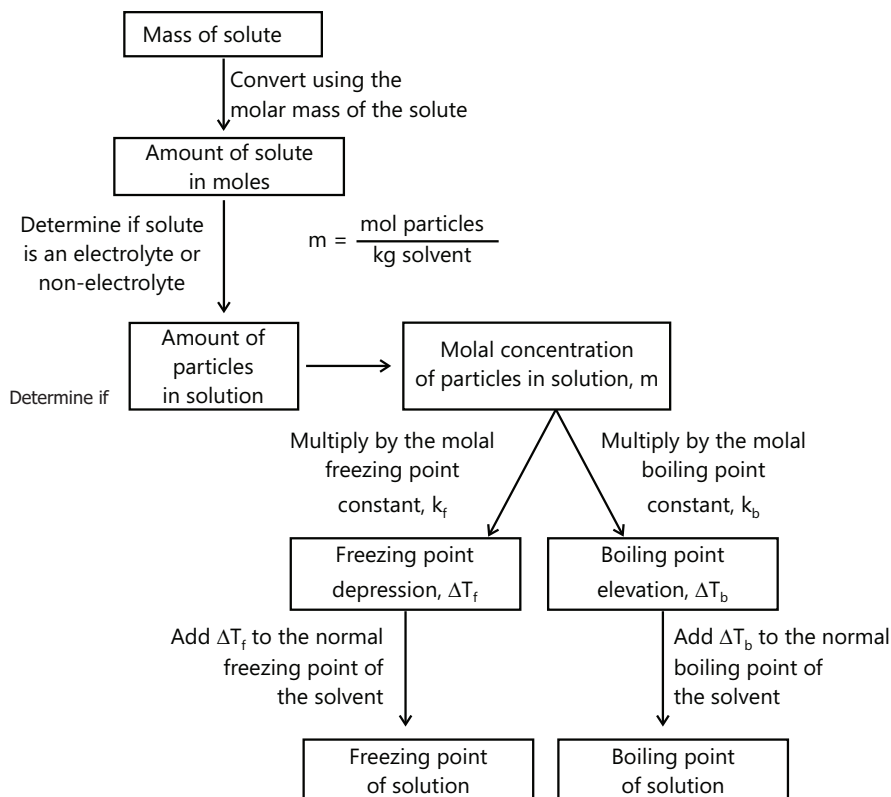


Figure 20.7

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, $\text{HOCH}_2\text{CHOHCH}_2\text{OH}$, 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

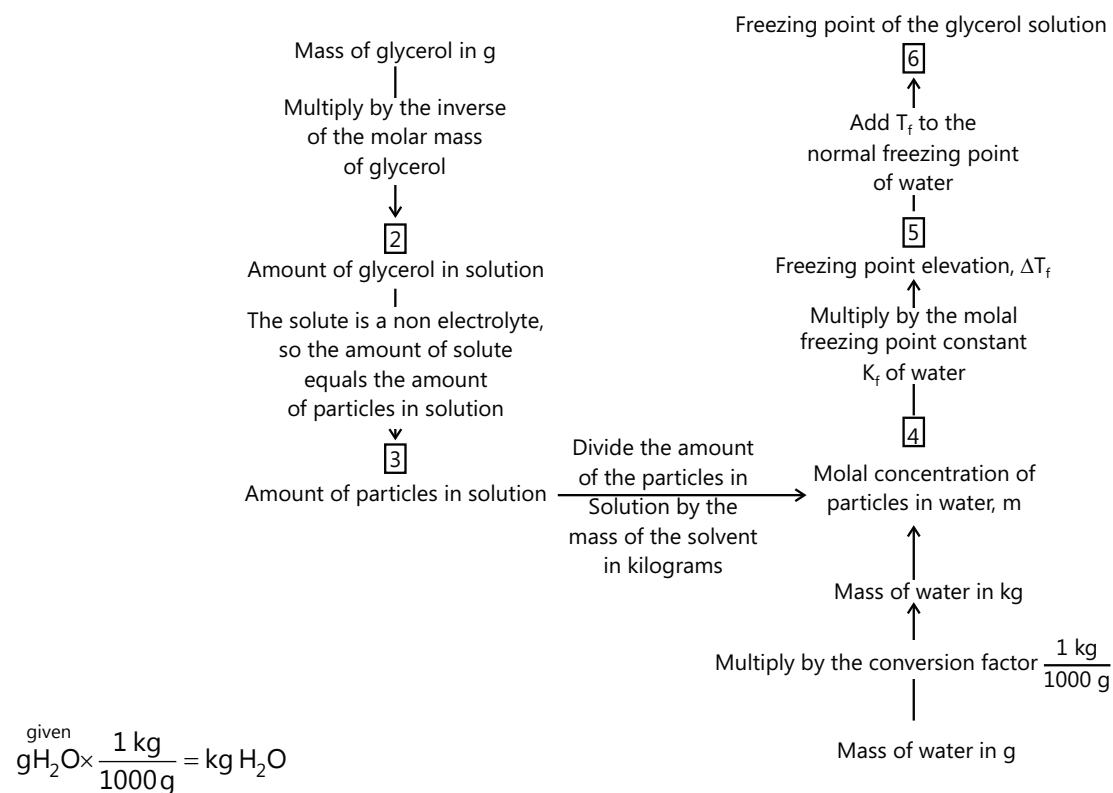
Items	Data
Identity of solute	Glycerol, $\text{HOCH}_2\text{CHOHCH}_2\text{OH}$
Particles per mole of solute	1 mol
Identity of solvent	Water
Freezing point of solvent	0.00°C
Mass of solvent	350 g
Mass of solute	210.0 g
Molar mass of solute	92.11 g/mol
Molal concentration of solute particles	?
Molal freezing 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 freezing constant for water to calculate the number of degrees the freezing point is lowered. Thereafter, add this negative value to the normal freezing point.



3. Compute

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

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

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

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

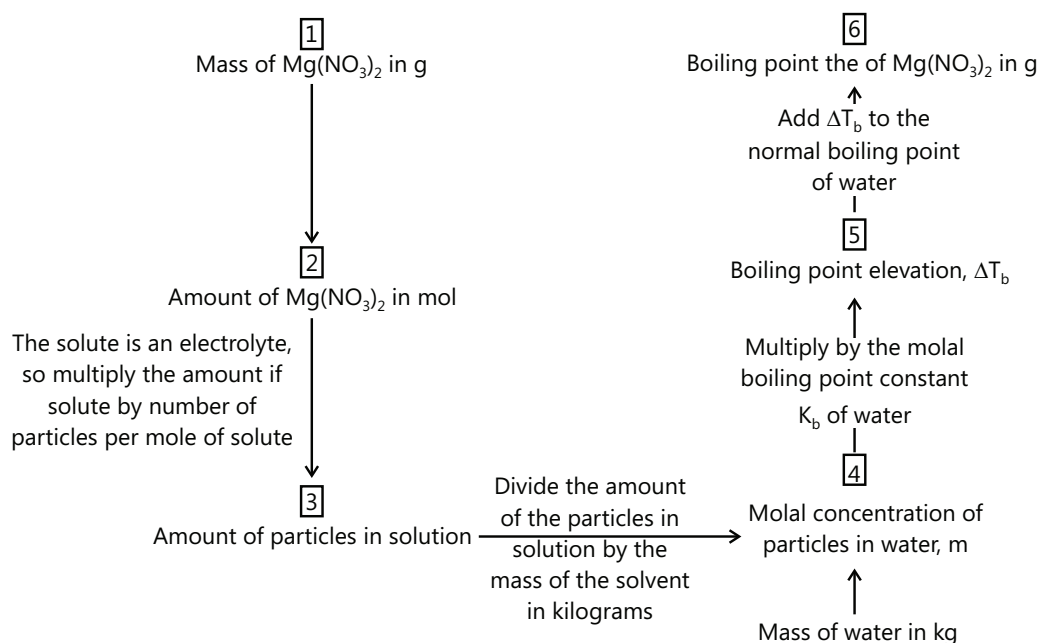
(i) What is given in the problem?	the formula and mass of solute and the mass of the water used
(ii) What are you asked to find?	the freezing point of the solution

Items	Data
Identity of solute	Magnesium nitrate
Equation for the dissociation of the solute	$\text{Mg}(\text{NO}_3)_2 \rightarrow \text{Mg}^{2+} + 2\text{NO}_3^-$
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 ₂ O
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.



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

$$\text{boiling point of H}_2\text{O} + \Delta t_b = t_b$$

$$100.0^\circ\text{C} + \Delta t_b = t_b$$

3. Compute

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

$$100.0^\circ\text{C} + 3.31^\circ\text{C} = 103.3^\circ\text{C}$$

4. Evaluate

(i) Are the units correct?	Yes, units canceled to give Celsius degrees.
(ii) Is the number of significant figure correct?	Yes, 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 $[35 \times 3]/150 \times 5 = (7/10) \times 5 = 3.5$, 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 constituents A and B. p_A^0 and P_B^0 = partial pressure of A and B, respectively
Relationship between Dalton's law and Raoult's law	$Y_A = \frac{X_A P_A^0}{P} = \frac{P_A}{P}$, $Y_B = \frac{X_B P_B^0}{P} = \frac{P_B}{P}$, where, Y_A and Y_B denotes mole fraction of components A and B in vapor phase
Lowering of vapor pressure	$\frac{P_A^0 - P}{P_A^0} = x_B$, relative lowering of vapor pressure = mole fraction of solute
Elevation in boiling point	$\Delta T_B = \frac{K_B W_B}{M_B \times W_A} \times 1000$
Depression in freezing point	$\Delta T_f = \frac{RT_f \times w_{\text{solute}}}{M_{\text{solute}} \times W_{\text{solvent}}} \times 1000$
Osmotic pressure	Osmotic pressure, $\pi = CRT$
van't Hoff factor, i	$i = \frac{\text{Normal molecular wt. (calculated value)}}{\text{Observed molecular wt. (experimental value)}}$
van't Hoff factor in case of association	For association, $\alpha = \frac{i-1}{n-1}$
van't Hoff factor in case of dissociation	For dissociation, $\alpha = \frac{i-1}{\frac{1}{n} - 1}$

Solved Examples

JEE Main/Boards

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

Sol: Mass of O_2 in mg = 6×10^{-3} g $\times 10^3$ mg/g = 6 mg
ppm of O_2 in 1030 g sea water

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

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

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

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

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

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

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

$w = 18 \text{ g}$ and $T = 293 \text{ K}$