Chapter 9

SOLUTION

SOLUTION

"Any mixture with only a single phase is called **homogeneous mixture or solution**."

Binary Solution:

"The solution which contains two components only, is called **binary solution**."

For example, mixture of sugar in water. Binary solution consists of solute and solvents.

Solvent and Solute:

"The substance which is present in large quantity in solution is called **solvent and the substance in small quantity is solute**."

In above example sugar is solute and water is solvent.

Concentration of Solution:

"The amount of solute dissolved in a unit volume of solution or solvent is called **concentration of solution**."

Dilute Solution and Concentrated Solution:

Solutions containing relatively lower concentrations of solute are called **dilute solutions**, whereas those containing relatively higher concentrations of solutes are called **concentrated solutions**.

CONCENTRATION UNITS

"The quantity of solute or solvent is generally measured in term of volume, mass, or moles, are usually called **concentration unit**."

The concentration of solution can be expressed by molarity, molality, percentage, and mole fraction.

1. Percentage Composition:

The amount of solute and solvent can be expressed in % age of four ways.

(a) Percentage weight/weight

(b) Percentage weight/volume

(c) Percentage volume/weight

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(d) Percentage volume/volume

(a) Percentage weight/weight:

"It is the weight of a solute dissolved per 100 parts by weight of solution."

5% w/w sugar solution will contain 5 g of sugar dissolved in 100 g of solution in water.

$$\% \text{ by weight} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

Example 1:

Calculate the percentage by weight of NaCl, if 2.0 g of NaCl is dissolved in 20 g of water.

Weight of NaCl = 2.0 g

Weight of solvent = 20.0 g

Weight of solution = 20 + 2 = 22 g

$$\% \text{ of NaCl by weight} = \frac{2.0\ g}{22.0\ g} \times 100$$

$$= 9.09\ \%$$

(b) Percentage weight/volume:

"It is the weight of solute dissolved per 100 parts by volume of solution."

10 g of glucose dissolved in 100 cm^3 of solution is 10% w/v solution of glucose. **The quantity of the solvent is not exactly known**. In such solutions, the total volume of the solutions is under consideration.

(c) Percentage volume/weight:

"It is number of cm^3 of a solute dissolved per 100 g of the solution."

If we dissolve 10 cm^3 of alcohol in water and the total weight of the solution is 100 g then it is 10% v/w solution of alcohol in water. In such type of solutions **we don't know the total volume of the solution**.

(d) Percentage volume/volume:

"It is the volume of a solute dissolved per 100 cm^3 of the solution."

This unit of concentration is best applicable to the solutions of liquids in liquids. A 12% alcohol beverage is 12 cm^3 of alcohol and 88 cm^3 of water is present. Total volume of solution will be 100 cm^3, if solution is ideal. If solution is non ideal, total volume of solution is not equal to the volume of solute and volume of solvent.

2. MOLARITY (M)

"The number of moles of solute dissolved per dm^3 of solution is called **molarity**."

It is denoted by "M".

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in } dm^3}$$

$$\text{No. of moles} = \frac{n}{v} = \frac{\text{Mass of solute}}{\text{Molecular mass of solute}}$$

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$$M = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution (dm}^3\text{)}}$$

For example:

One molar glucose contains 180 g of $(C_6H_{12}O_6)$ glucose dissolved per dm^3 of solution. One molar (1M) $C_{12}H_{22}O_{11}$ sucrose contains 342 g of sucrose per dm^3 of solution. This solution is **prepared in measuring** flask. Measuring flask of different volumes are available.

However, 1M $C_6H_{12}O_6$ and 1M $C_{12}H_{22}O_{11}$ have same number of solute particles but volume of solvent is different. Volume of solvent is greater in 1M $C_6H_{12}O_6$ and less in 1M $C_{12}H_{22}O_{11}$.

To calculate the volume of solvent we need to know the density of solute.

Example 2:

Calculate the molarity of a solution containing 20.7 g of K_2CO_3 dissolved in 500 cm^3 of the given solution.

Solution:

Mass of $K_2CO_3 = 20.7$ g

Molar mass of $K_2CO_3 = 138$ g mol^{-1}

Volume of solution $= 500\ cm^3 = 0.5\ dm^3$

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution (dm}^3\text{)}}$$

$$= \frac{20.7\text{ g}}{138\text{ g mol}^{-1}} \times \frac{1}{0.5\text{ dm}^3}$$

$$= 0.3\text{ mole dm}^{-3} = 0.3\text{ M}$$

MOLALITY (m)

"The number of moles of solute dissolved per kilogram of solvent is called **molality**."
It is denoted by "m".

$$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent (kg)}}$$

$$\text{No. of moles} = \frac{n}{w} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}}$$

$$m = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent (kg)}}$$

For Example:

One molar glucose contains 180 g of $(C_6H_{12}O_6)$ present [in one kg of water (solvent)]. Total mass of solution is (1000 g solvent + 180 g solute) 1180 g. In this case to calculate volume of solution, we need density of solution.

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1m NaOH contains 40 g of NaOH in 1 kg of water.

1m sucrose ($C_{12}H_{22}O_{11}$) contains 342 g of solute in 1 kg of solvent.

Example 3:

What is the molality of a solution prepared by dissolving 5 g of toluene (C_7H_8) in 250 g of benzene.

Solution:

Mass of toluene = 5 g

Mass of benzene = 250 g

Molar mass of toluene = $12 \times 7 + 1 \times 8 = 92$

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent (kg)}}$$

$$= \frac{5\text{ g}}{92\text{ g of mol}^{-1}} \times \frac{1}{0.250\text{ kg}}$$

$$= \frac{5}{92 \times 0.25} \text{ mole kg}^{-1}$$

$$= 0.217 \text{ mole kg}^{-1} = 0.217 \text{ m}$$

Molality of solution does not change by changing temperature. However, molarity of solution decreases by increasing temperature. Volume of liquid is affected by temperature but mass is not affected by variation of temperature.

TABLE

Comparison of Molarity and Molality:	
Molarity (1M)	**Molality (1m)**
1. The number of moles of solute dissolved per dm^3 of solution.	1. The number of moles of solute dissolved per kg of solvent.
2. It is denoted by "M".	2. It is denoted by "m".
3. Quantity of solvent is less than molal solution so it is concentrated than molal solution with values.	3. Quantity of solvent is greater than molar solution so it is dilute as compared to molar solution with same values.
4. Molarity changes by changing the temperature because volume or solvent is affected.	4. Molality does not changes by changing the temperature because mass of solvent is not affected.
5. **Example:**	5. **Example:**

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1M glucose contain 1 mole of $C_6H_{12}O_6$ (180 g) per dm^3 of solution.	1m glucose contain 1 mole of $C_6H_{12}O_6$ (180 g) per kg of solvent.

3. Mole Fraction (x):

"The ratio of number of mole of a component to the total number of moles in a solution is called **mole fraction**."

It is denoted by "x".

The important features of mole fraction is

(i) This unit of concentration may be used for any solutions of gas in gas, liquid in liquid, and liquid in solid.

(ii) This unit of also applicable when more than two components are present in the solution.

(iii) There are no formal units of mole fraction. Anyhow we sometimes multiply mole fraction by 100 to get mole percent.

Let there be many components A, B and C making a solution. The number of moles are n_A, n_B and n_C respectively. If the mole fraction of A, B and C are denoted by X_A, X_B and X_C respectively then.

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

$$X_B = \frac{n_B}{n_A + n_B + n_C}$$

$$X_C = \frac{n_C}{n_A + n_B + n_C}$$

The **sum of the mole fractions** of all the components of a solution must be equal to **one**.

$$X_A + X_B + X_C = 1$$

$$\text{Mole percent} = \frac{\text{Mole of one component}}{\text{Total moles}} \times 100$$

In the case of mixture of gases, one can determine the mole fraction from the partial pressure data of the mixture. Hence

$$X_A = \frac{P_A}{P_A + P_B + P_C}$$

$$X_B = \frac{P_B}{P_A + P_B + P_C}$$

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$$X_C = \frac{P_C}{P_A + P_B + P_C}$$

$$\text{Mole fraction of any gas} = \frac{\text{Partial pressure of that gas}}{\text{Total pressure of the mixture of gases}}$$

Example 4:

Calculate the mole fraction and mole percent of each component in a solution having 92 g of ethyl alcohol, 96 g of methyl alcohol and 90 g of water.

$$\text{No. of moles of the substance} = \frac{\text{Mass of grams of the substance}}{\text{Molecular mass}}$$

$$\text{No. of moles of ethyl alcohol} = \frac{92\text{ g}}{46\text{ g mol}^{-1}} = 2\text{ moles}$$

$$\text{No. of moles of methyl alcohol} = \frac{96\text{ g}}{32\text{ g mol}^{-1}} = 3\text{ moles}$$

$$\text{No. of moles of water} = \frac{90\text{ g}}{18\text{ g mol}^{-1}} = 5\text{ moles}$$

$$X_{\text{ethyl alcohol}} = \frac{2}{2+3+5} = \frac{2}{10} = 0.2$$

$$X_{\text{methyl alcohol}} = \frac{3}{2+3+5} = \frac{3}{10} = 0.3$$

$$X_{H_2O} = \frac{5}{2+3+5} = \frac{5}{10} = 0.5$$

Mole % of alcohol = $0.2 \times 100 = 20$

Mole % of $CH_3OH = 0.3 \times 100 = 30$

Mole % of $H_2O = 0.5 \times 100 = 50$

4. PARTS PER MILLION (ppm)

"The number of parts (by mass or volume) of a solute per million parts (by mass or by volume) of the solution is called **ppm**."

This unit is used for very low concentrations of solutions, e.g. to express the impurities of substances in water.

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

Example 5:

Seawater has 5.65×10^{-3} g of dissolved oxygen is one kg of water. Calculate the concentration of oxygen in seawater in parts per million.

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Solution:

$$\text{ppm of oxygen in seawater} = \frac{5.65 \times 10^{-3}\ \text{g}}{1000\ \text{g}} \times 10^{6}$$

$$= 5.65\ \text{ppm}$$

INTER–CONVERSION OF VARIOUS CONCENTRATION UNITS OF SOLUTION

Sometimes we get prepared solutions form the chemical supply houses. For example, we are working with a solution whose molarity is given by the supplier, but we need to know its molarity or w/w percentage. For such purpose, we need to convert one unit of concentration into other. These conversions are usually done if we known the formula masses and the densities of the solutes or solutions.

Example 6:

Percentage to Molality:

Calculate the molality of 8% w/w NaCl solution.

Solution:

8% w/w NaCl solution means that 8 g of NaCl is dissolved in 100 g of solutions.

So, mass of water in the solution = 100 – 8 = 92 g.

$$\text{Mass of solvent in kg} = \frac{92}{1000} = 0.092\ \text{kg}$$

$$\text{Molality} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent (kg)}}$$

$$= \frac{8\ \text{g}}{58.5\ \text{g mol}^{-1}} \times \frac{1}{0.092\ \text{kg}}$$

$$= 1.487\ \text{mole kg}^{-1}$$

Example 7:

Percentage to Molarity:

Hydrochloric acid available in the laboratory is 36% (w/w). The density of HCl solutions is 1.19 cm^{-3}. Determine the molarity of HCl solution.

Solution:

Mass of HCl = 36 g

Mass of solution = 100 g

$$\text{Volume of solution} = \frac{\text{mass}}{\text{density}}$$

$$= \frac{100\ \text{g}}{1.19\ \text{g cm}^{-3}} = 84.03\ \text{cm}^{3}$$

$$\text{Volume in dm}^{3} = \frac{84.03\ \text{cm}^{3}}{1000} = 0.084\ \text{dm}^{3}$$

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$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution (dm}^3\text{)}}$$

$$= \frac{36\ \text{g}}{36.5\ \text{g mol}^{-1}} \times \frac{1}{0.084\ \text{dm}^3}$$

$$= 11.73\ \text{mole dm}^{-3} \text{ or } 11.73\ \text{M}$$

Example 8:

Molarity to Percentage:

9.2 molar $HClO_4$ is available from the market. The density of this solution is 1.54 cm^{-3}. What is the percentage by weight of $HClO_4$.

Solution:

Molarity of $HClO_4 = 9.2\ \text{mole dm}^{-3}$

Mass = v x d

Mass of 1000 cm^3 solution = 1000 cm^3 x 1.54 g cm^{-3}

= 1540 g

Molar mass of $HClO_4 = 100.5\ \text{g mol}^{-1}$

Mass = molar mass x mole

Mass of $HClO_4 = 100.5\ \text{g mol}^{-1} \times 9.2\ \text{mol dm}^{-3}$

$= 924.6\ \text{g dm}^{-3}$

Mass of $H_2O = 1540\ \text{g} - 924.6\ \text{g} = 615.4\ \text{g}$

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

$$\%\ \text{of } HClO_4 \text{ by mass} = \frac{924.6\ \text{g}}{1540\ \text{g}} \times 100 = 60.013\%$$

$$\%\ \text{of } H_2O \text{ by mass} = \frac{615.4\ \text{g}}{1540\ \text{g}} \times 100 = 39.99\%$$

TYPES OF SOLUTIONS

There are nine types of solution on the bases of physical states of solutes and solvents. These types are given in the Table.

TABLE

Common Types and Examples of Solutions			
No.	**State of Solute**	**State of Solvent**	**Example**
1.	Gas	Gas	Air
2.	Gas	Liquid	O_2 in water, CO_2 in water (aerated water, soft drinks, fizzy drinks, soda water).
3.	Gas	Solid	H_2 absorbed by palladium (occlusion).
4.	Liquid	Gas	Mist, fog, clouds, liquid air pollutant.
5.	Liquid	Liquid	Alcohol in water, milk.

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6.	Liquid	Solid	Mercury in silver (amalgam), butter, cheese.
7.	Solid	Liquid	Sugar in water, jellies, paints.
8.	Solid	Gas	Dust particles or smoke in air.
9.	Solid	Solid	Metal alloy (brass, bronze, German silver) pearls, opals, carbon in iron (steel).

1. SOLUTION OF SOLIDS IN LIQUIDS

When a solid comes in contact with a suitable liquid, it dissolves forming a solution i.e. a homogenous mixture. This process of dissolution can be explained in terms of attraction between the particles of a solute and that of a solvent. The molecules or ions in solids are arranged in such a regular pattern that the inter–molecular or inter–ionic forces are at a maximum. The process of dissolution is to overcome these forces of attraction holding together the solute molecules or ions in the crystal lattice, by the solute–solvent forces.

The principle of solubility is that "**like dissolved like**". Polar solutes are soluble in polar solvents while non–polar solutes soluble in non–polar solvents.

(a) Molecular Crystals are Soluble in Non–Polar Solvents:

In molecular crystals, the inter–molecular forces of attraction are either dipole–dipole or London dispersion type, so are relatively weak and can easily be overcome. Non–polar or less polar molecular crystals usually dissolve in non–polar solvents like benzene.

(b) Ionic–Crystals and Highly Polar Crystals are Soluble in Polar Solvents:

In the crystal lattice, the inter–molecular or inter–ionic forces of attraction between highly polar molecules or ions are quite strong, hence the polar solids fail to dissolve in non–polar solvents. These strong electrostatic forces cannot be overcome or shattered by the weak solute–solvent attractions. Take the case of cane sugar, due to hydrogen bonding, it has tightly bonding molecules, so it will not be dissolved by solvents like kerosene oil, petrol, benzene, etc. but will be dissolved readily in water because water attracts sugar molecules almost in the same way as the sugar molecules attract one another.

The inter–ionic forces of attraction are very strong in ionic solids. Equally strong polar solvents are needed to dissolve them. Such solids cannot be dissolved by moderately polar solvents like acetone. A moderate polar solvent, fails to dissolve ionic solids like NaCl.

2. Solution of Liquids in Liquids:

The solutions of liquids in liquids may be divided into three classes.

1. Practically Immiscible Liquids:

Those liquids which do not dissolve into each other in any proportion are immiscible.

Example:

(i) Water and Benzene

(ii) Carbon disulphide and water

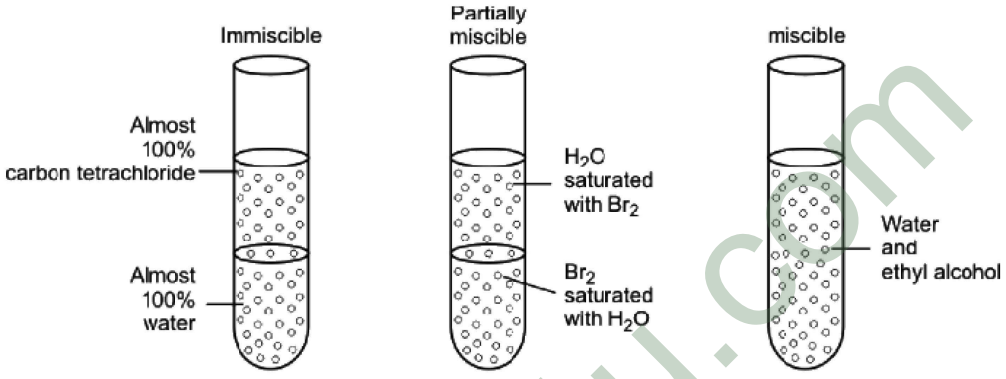
(iii) Carbon tetrachloride and water

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2. Completely Miscible Liquids:

"Such liquids are miscible in all proportions."

Liquids like alcohol and water or alcohol and ether mix in all proportions. However, the properties of such solutions are not strictly additive. Generally, the volume decrease on mixing but in some cases it increase. Heat may be evolved or absorbed during the formation of such solutions. These types of solutions can usually be separated by fractional distillation.



Immiscible, partially miscible, and miscible liquids

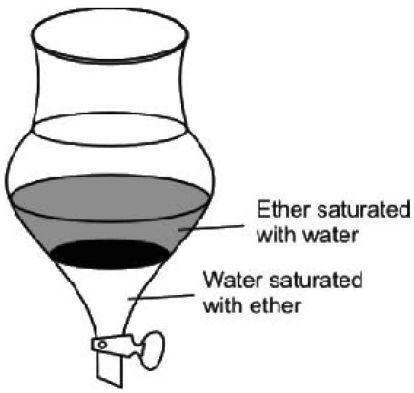
Example:

(i) Water and ethyl alcohol
(ii) Ethyl alcohol and ether
(iii) Benzene and toluene

3. PARTIALLY MISCIBLE LIQUIDS

"The liquid which dissolves into another liquid upto a limited extent is called **partially miscible liquid**."

For example, when ether and water are shaken together in separating funnel and layers allowed to separate. Some ether is present in water layer (1.2%). Presence of water in ether can be seen by igniting it. some water vapours are present in ether layer (6.5%). Presence of water vapour in ether layer can be seen, by dissolving some anhydrous $CuSO_4$ in this layer. $CuSO_4$ is not soluble in pure ether.



Each liquid layer is a saturated solution of the other liquid. Such solutions are called **conjugate solutions**. The mutual solubility of these conjugate solutions is affected by temperature changes. Typical example of such systems are:

(i) Phenol–water system

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(ii) Tri–ethylamine–water system

(iii) Nicotine–water system

PHENOL–WATER SYSTEM

If equal volumes of water and phenol are mixed together they show partial miscibility. It has been observed that around room temperature, phenol will dissolve in a lot of water giving us the upper layer and water will dissolve in a lot phenol giving us the lower layer.

As 25°C the **upper layer is 5% solution of phenol in water and the lower layer is 30% water** in phenol. The lower layer has a greater density due to greater percentage of phenol. Water acts as a solute in the lower layer while phenol is a solute in the upper layer. When the temperature of water–phenol system is increased, the compositions of both layers change. Water starts traveling from upper to the lower layer and phenol travels from lower to the upper layer. When the temperature of this system approaches **65.9°C**, a homogenous mixture of two components is obtained. This homogeneous mixture contains 34% phenol and 66% water.

"The temperature at which two conjugate solutions merge into one another, is called **critical solution temperature or upper consulate temperature**."

Critical solution temperature for water–phenol system is 65.9°C.

Some other partially miscible pairs of liquids have their own consulate temperature with definite compositions. For example, water–aniline system has a single layer at 167.0°C with 15% water. Methanol–cyclohexane system has consulate temperature of 49.1°C with 29% methanol.

Ideal and Non–Ideal Solutions:

When two or more than two liquid substances are mixed, the solutions may be ideal or non–ideal. To distinguish between such solutions we look at the following aspects:

TABLE

Ideal Solution	Non–Ideal Solution
1. The force of interaction between the molecules of different components are same as they were in the pure state. $A-A,\ B-B = A-B$	1. The force of interaction between the molecules of different components are not same as they were in the pure state. $A-A,\ B-B \neq A-B$
2. Volume of solution is sum of the volumes of solute and solvent and change in volume is zero, $\Delta V = 0$. $V_{solvent} + V_{solute} = V_{solution}$	2. Volume of solution is sum of the volumes of solute and solvent and change in volume is not zero, $\Delta V \neq 0$. $V_{solvent} + V_{solute} \neq V_{solution}$
3. Ideal solutions have zero enthalpy change as their heat of solution, $\Delta H = 0$.	3. Non–ideal solutions have endothermic or exothermic enthalpy as their heat of solution, $\Delta H \neq 0$.
4. Temperature does not change, when solution is formed.	4. Temperature increases or decreases, when solution is formed.
5. Ideal solution obey the Raoult's law.	5. Non–ideal solution does not obey the

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$P = P^oX_1$	Raoult's law. $P = P^oX_1$
6. Ideal solutions obey Vant-Hoff's equation $\pi v = n_2RT$.	6. Non-ideal solutions do not obey Vant-Hoff's equation.
Example: (i) Benzene and ether (ii) Chlorobenzene and bromobenzene.	**Example:** (i) Acetone–water (ii) Ethanol–hexane.

RAOULT'S LAW

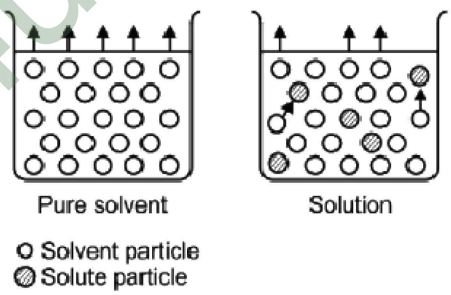
(When solute in non–volatile and solvent is volatile)

(a) Vapour pressure of a solvent above solution is equal to the product of vapour pressures of pure solvent and mole fraction of solvent in a solution.

Mathematically it is can be written as

$$p = p^o x_1 \qquad (1)$$

Where p^o is vapour pressure pure of solvent p is vapour pressure of solvent in solution x_1 is mole fraction of solvent. p is always less than P^o, because surface area for the solvent decreases in solutions form. Some solute particles are also present at the surface, which are non–volatile, so $P < P^o$.



(b) This law can be written as $\Delta P = P^o X_2$. **Lowering of vapour pressure is directly proportional to mole fraction of solute**. We know that $x_1 + x_2 = 1 \qquad x_1 = 1 - x_2$

Putting the value of x_1 in Equation (1).

$$p = p^o (1 - x_2)$$

or $$p = p^o - p^o x_2$$

or $$p^o - p = p^o x_2$$

or $$\Delta p = p^o x_2 \quad \text{or} \quad \Delta p \propto x_2 \qquad (2)$$

(c) "Relative lowering of vapour pressure $\left(\frac{\Delta p}{p^o}\right)$ is equal to the mole fraction of solute."

We know that

$$\Delta p = p^o x_2$$

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by rearranging $\frac{\Delta p}{p^o} = x_2$ (3)

The relative lowering of vapour pressure:

(i) is independent of the temperature.

(ii) depends upon the concentration of solute.

(iii) is constant when equimolecular proportions of different solutes are dissolved in the same mass of same solvent.

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Example 9:

The vapour pressure of water of 30°C is 28.4 torr. Calculate the vapour pressure of a solution containing 70 g of cane sugar ($C_{12}H_{22}O_{11}$) in 1000 g of water at the same temperature.

Solution:

No. of moles of $C_{12}H_{22}O_{11}$ $(n_2) = \frac{70\text{ g}}{342\text{ g/mol}} = 0.20$ moles

No. of moles of H_2O $(n_1) = \frac{1000\text{ g}}{18.02\text{ g/mol}} = 55.49$ moles

Total no. of moles $= 0.20 + 55.49 = 55.69$

Mole fraction of H_2O $(x_1) = \frac{n_1}{n_1 + n_2}$

$= \frac{55.49}{55.69} = 0.9964$

Applying the formula $= p = p^o x_1$

$= (28.4)\ (0.9964) = 28.29$ torr

So, vapour pressure of solution $= 28.29$ torr.

RAOULT'S LAW

When both components are volatile:

Raoult's law can be applied to understand the relationship between mole fractions of two volatile components and their vapour pressures before making the solution and after making the solution. Consider two liquids 'A' and 'B' with vapour pressures p_A^o and p_B^o in the pure state at a given temperature. After making the solution, the vapour pressures of both liquids are changed. Let the vapour pressures of these liquids in solution state be p_A and p_B with their mole fractions x_A and x_B respectively.

Applying Raoult's law to both components

$p_A = p_A^o X_A$

$p_B = p_B^o X_B$

$P_t = p_A + p_B = p_A^o X_A + p_B^o X_B$

Since $X_A + X_B = 1$

$X_B = 1 - X_A$

$P_t = p_A^o X_A + p_B^o (1 - X_A)$

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$$P_t = p_A^o X_A + p_B^o - p_B^o X_A$$

$$P_t = p_A^o X_A - p_B^o X_A + p_B^o$$

$$P_t = (p_A^o - p_B^o) X_A + p_B^o \qquad (4)$$

Equation (4) is a straight line. The equation of straight line is $y = mx + c$. Where y and x are variable, m is slope and c is constant.

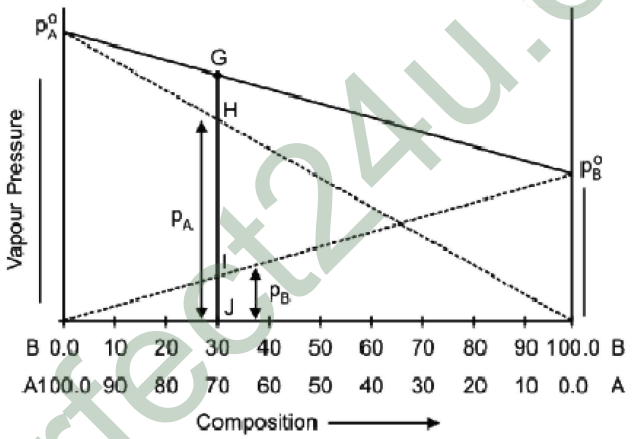
$$P_t = (p_A^o - p_B^o) X_A + p_B^o$$

$$\uparrow \quad \uparrow \quad \uparrow \quad \uparrow$$

$$y \quad m \quad x \quad c$$

If we plot a graph between P_t at y–axis and, X_A or $(1 - X_B)$ at x–axis, a straight line is obtained. Liquid A is more volatile than liquid B.

Only those pairs of liquids give straight lines which form ideal solutions. So Raoult's law is one of the best criterion to judge whether a solution is ideal or not.



Graph between composition and vapour pressure

All the possible solutions of two components A and B have their vapour pressures on the straight line connecting p_A^o with p_B^o. All such solutions will be ideal. Each point on this straight line represents the vapour pressure of a solution, at a given temperature, with the corresponding contribution of both the components A and B. The two dotted lines represent the partial pressures of the individual components of solution. They show the increase of vapour pressure of component with increase in its mole fraction in solution.

In order to explain it, consider a point G on the straight line. This point represents the vapour pressure of solution with 30% contribution of the component B and 70% of A. Since A is more volatile component, so its contribution towards the vapour pressure of solution is represented by p_A, the contribution of the less volatile component B is represented by p_B. Similarly we can calculate the relative contributions of A and B towards the total vapour pressure of solution by taking other points along the line joining p_A^o to p_B^o.

The total vapour pressure of the solution (P_t) corresponding to the point G will be equal to the sum of the vapour pressures of the individual components $(p_A + p_B)$ as shown in Figure.

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Vapour Pressures of Liquid – Liquid Solutions:

The study of vapour pressures of miscible liquids is of great help in the separation of liquids by fractional distillation.

Binary mixtures of miscible liquids may be classified as (i) Ideal (ii) Non–ideal or real solutions.

The vapour pressures of solutions provide a simple picture about their behaviour. Let us consider the vapour pressures of ideal and real solutions.

(i) IDEAL SOLUTIONS

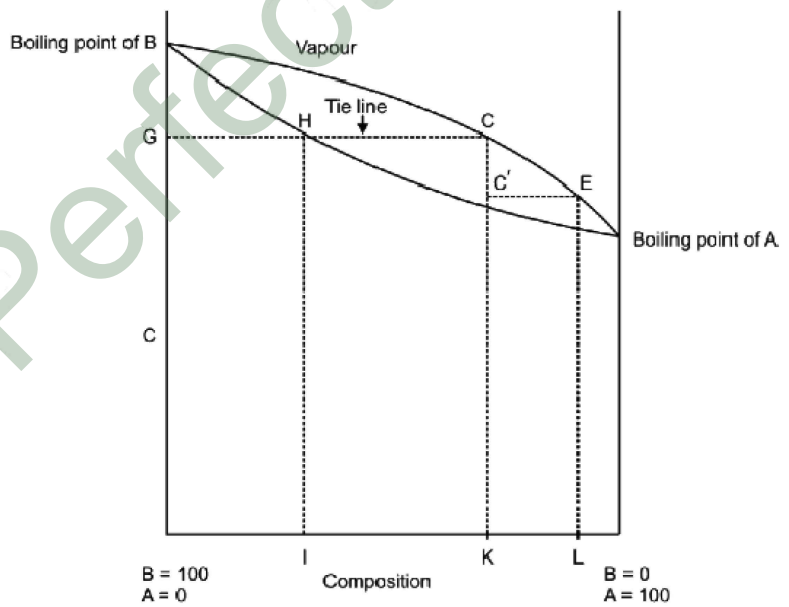
An ideal solution is that which obeys Raoult's law."

Some typical ideal solution forming liquid pairs are: benzene–toluene, benzene–ether, chlorobenzene–bromobenzene, ethyl iodide–ethyl bromide, etc.

FRACTIONAL DISTILLATION OF IDEAL MIXTURE OF TWO LIQUIDS

Liquid–vapour phase diagram at constant pressure is important to study the fractional distillation. Fractional distillation is a technique by which different liquids are separated from each other on the basis of their different boiling points.

Let us have two liquids A and B in mixture, which forms a completely miscible solution. A is more volatile and has less boiling point, while B is less volatile and has greater boiling point. If we plot a boiling point of liquid mixture against its composition and the composition of vapour in contact with it, we get two separate curves of each type of solutions.



Constant-pressure phase diagram showing composition of both liquid and vapour

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Consider the temperature corresponding to point G. It meets liquid curve at point H and vapour curve at point C. This CH curve is called **tie line**. Composition of liquid mixture correspond to point H is shown at point I. At point I the percentage of have high percentage of A and less percentage of B. These vapours rise in fractional column, its temperature decreases until it condenses. This temperature drop is represented by vertical line CK in the phase diagram. At point C', a new equilibrium is established between the condensate descends the column while the vapour ascends. Thus, at various stages in the column, the descending liquid and ascending vapours are in equilibrium. These equilibrium are represented by tie lines. As the vapours rise in the column through each successive equilibrium, they become richer in more volatile component A. Eventually, they pass out the column at the top are condensed and collected. At the same time, liquid in the flask becomes richer in the less volatile component and consequently its boiling point increases. So we can completely separate the liquid mixture by fractional distillation.

"The liquid mixture which distil with a change in composition are called a **Zeotropic mixture**."

For example, methyl alcohol water solution can be separated by fractional distillation.

Fractional distillation technique is also used

(1) In the refining of petroleum.

(2) Manufacture of O_2, N_2 and noble gases from liquid air.

(3) Production of whisky and other alcoholic products.

(ii) Non–Ideal Solutions (Azeotropic Mixtures):

Many solutions do not behave ideally as they show deviations from Raoult's law due to differences in their molecular structures i.e. size, shape and inter–molecular forces. Formation of such solutions is accompanied by changes in volume and enthalpy. The vapour pressure deviations may be positive or negative in such solutions.

AZEOTROPIC MIXTURE

"The liquid mixture which boils at constant temperature and distills over without change in composition at any pressure like a chemical compound is called **azoetropic mixture**."

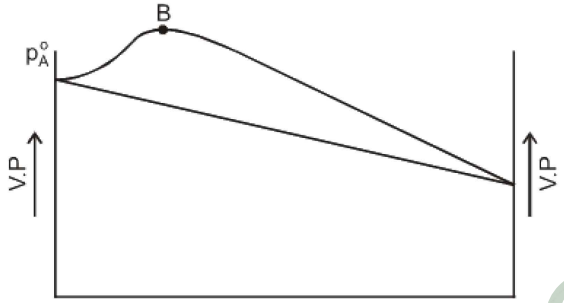
(a) POSITIVE DEVIATION

When the vapour pressure of mixture is greater than that predicted by the Raoult's law, exhibit a positive deviation. When **attractive forces** between the solute molecules or between solvent molecules, neither the solute nor the solvent held as tightly in the solution as they are in pure state. The escaping tendency of each is therefore greater in the solution than in the solute or solvent alone. As a result, **partial pressures** of both of them over the solution are **greater** than predicted by the Raoult's law.

The liquids which have greater vapour pressure have **low boiling points**. The liquid mixtures which have highest vapour pressure have lowest boiling points. On distilling this type of solution, the first fraction will be constant boiling mixture (azoetropic mixture) having a fixed

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composition. For such mixture, it is impossible to bring about complete separation of components by fractional distillation. Ethanol–water is an example of positive deviation. The composition which have 95% alcohol by volume is a azoetropic mixture and 5% water cannot be removed from it by fractional distillation.



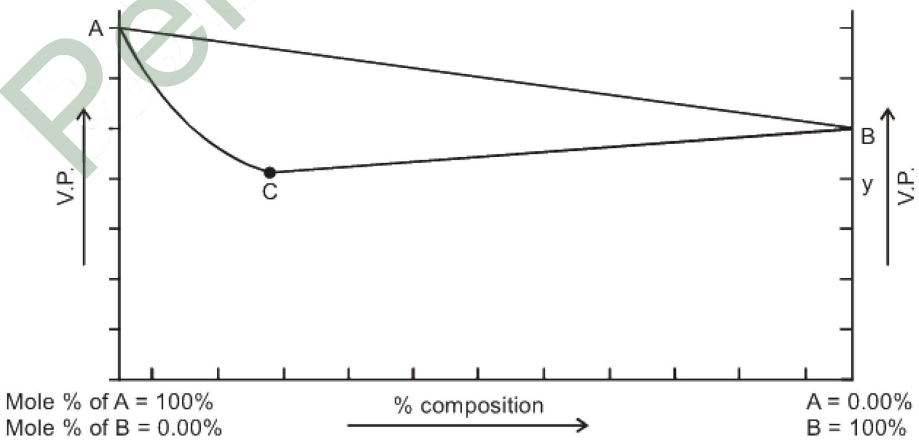
A pair of components showing positive deviation from Raoult's law.

NEGATIVE DEVIATION

"When the vapour pressure of liquid mixture is less than the predicted value of Raoult's law, it shows negative deviation."

When solute–solvent **interaction is stronger** than solute–solute or solvent–solvent interaction opposite effect is seen. Each substance in the presence of other is held more tightly then in the pure material and their **partial pressure are less**, as predicted by the Raoult's law. Doted line in the graph shows the ideal behaviours. The liquid mixture which have lowest vapour pressure have **highest boiling points**. It is also impossible to separate completely such mixtures by fractional distillation.

We can give the example of hydrochloric acid solution in water for this type of solutions. HCl forms an azeotropic mixture with water which boils at $110^{\circ}C$ and containing 20.24% of the acid. Similarly figure shows that the pair of liquids showing the negative deviation form azeotropic mixture with maximum boiling point corresponding to G in comparison with pure components.



A pair of components showing negative deviation from Raoult's law.

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TABLE

Summary of Solution Properties				
Relative attractive forces	**$\Delta H_{(sol)}$**	**Temp. change when solution is formed**	**Deviation from Raoult's laws**	**Volume Change**
A – A, B – B = A – B	Zero	None	None (ideal sol)	$\Delta V = 0$
A – A, B – B < A – B	Negative (exothermic)	Increase	Negative	Slightly decreases
A – A, B – B > A – B	Positive (endothermic)	Decrease	Positive	Slightly increases

SOLUBILITY AND SOLUBILITY CURVE

Solubility:

"The concentration of the solute in solution, when it is in equilibrium with solid substance, at particular temperature is called **solubility**."

Whenever a solid solute is put in a liquid solvent then the molecules or ions breakaway from the surface of the solid and pass into the solvent. These particles of solid are free to diffuse throughout the solvent to give a uniform solution. The solute and solvent molecules are constantly moving about in the solution phase because of kinetic energy possessed by them. This process is called **dissolution**.

Some of the particles of the solute come back towards the solid due to collisions. These molecules or ions are entangled in its crystal lattice and get deposited on it. This is called **re–crystallization or precipitation**.

If excess solid is present in the solution than the rate of dissolution and rate of crystallization becomes equal. This is the state of dynamics equilibrium.

Dissolution $\rightleftharpoons$ Crystallization.

The concentration of the solute at equilibrium with the solution is constant for a particular solvent and at a fixed temperature. The solution thus obtained is called **saturated solution of the solid substance** and the concentration of this solution is termed as its solubility.

Unit of Solubility:

Solubility is expressed in terms of number of grams of solute in 100 g of solvent. At a particular temperature saturated solution of NaCl in water at $0^{o}C$ contains 37.5 g of NaCl in 100 g of water. Similarly the solubility of $CuSO_4$ in water at $0^{o}C$ is 14.3 g/100 g while at $100^{o}C$ it is 75.4 g/100 g.

Determination of Solubility:

To determine the solubility of substance, a saturated solution of a solid is prepared at a constant temperature. Then this solution is filtered. A known volume of this solution is evaporated in a china dish and from the mass of the residue, the solubility can be calculated.

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Effect of Temperature on Solubility:

Substance	Temperature °C					
	0°	20°	40°	60°	80°	100°
NaCl	35.7	35.9	36.4	37.1	38.0	39.2
$NaNO_3$	73	87.6	102	122	148	180
KCl	28.0	34.2	40.1	45.8	51.3	56.3
KI	128	144	162	176	192	206
KNO_3	13.9	31.6	61.3	106	167	245
Li_2CO_3	1.54	1.33	1.17	1.01	0.85	0.72
$AgNO_3$	122	216	311	440	585	733
$Ba(OH)_2$	1.67	3.89	8.22	20.9	101	
$C_{12}H_{22}O_{11}$	179	204	238	287	362	487
$Ca(OH)_2$	0.189	0.173	0.141	0.121	0.094	0.07

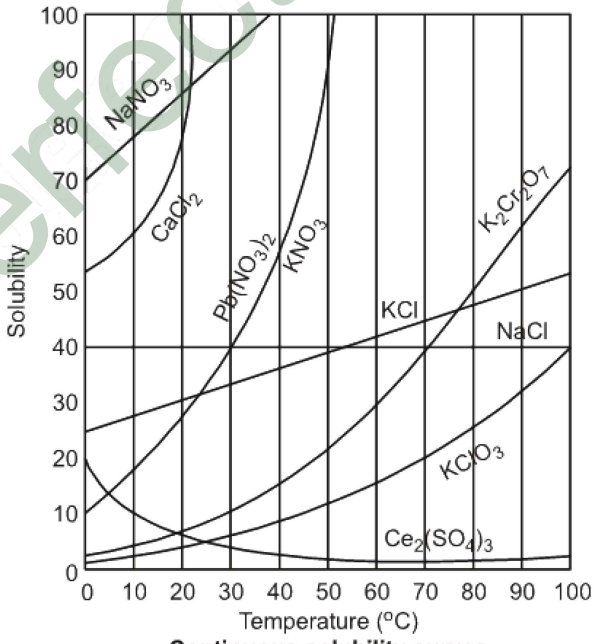
SOLUBILITY CURVE

Temperature has a marked effect on the solubility of many substances. A curve between solubility and temperature is called **solubility curve**. There are two types of solubility curves.

1. Continuous solubility curves 2. Discontinuous solubility curves

1. Continuous Solubility Curves:

Continuous solubility curves don't show breaks anywhere. According to figure $KClO_3$, $K_2Cr_2O_7$, $Pb(NO_3)_2$ and $CaCl_2$ are showing continuous solubility curves.



Continuous solubility curves

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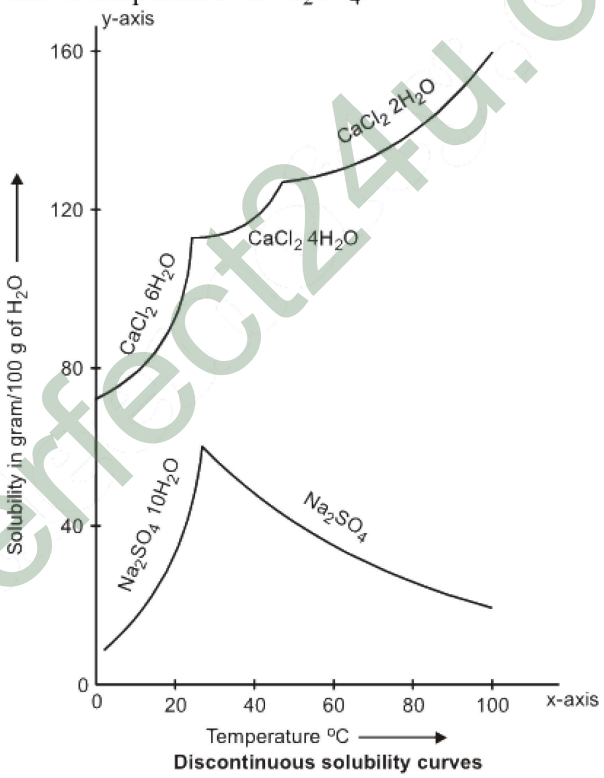
The solubility curves of KCl, NaCl and $NaNO_3$ give the straight lines. NaCl shows a very small change of solubility from 0^oC to 100^oC increase of temperature.

$Ce_2(SO_4)_3$ shows the exceptional behaviour whose solubility decreases with the increase in temperature and becomes constant from 40^oC onwards. Anyhow, it shows continuous solubility curve.

2. Discontinuous Solubility Curves:

Sometimes the solubility curves shows sudden changes of solubilities and these curves are called **discontinuous solubility curves**. The best examples in this reference are Na_2SO_4 $10H_2O$, $CaCl_2$ $6H_2O$. Actually these curves are combination of two or more solubility curves. At the break, a new solid phase appears the another solubility curve of that new phase begins.

For example, in case of **Glauber's salt (Na_2SO_4 $10H_2O$)** solubility increase upto 32.4^oC, it loses water of crystallization and changes to anhydrous Na_2SO_4 32.4^oC is the transition temperature between Na_2SO_4 $10H_2O$ and Na_2SO_4. Above this point, curve for Na_2SO_4 starts and represents the effect of rise of temperature on Na_2SO_4.



Discontinuous solubility curves

Fractional Crystallization:

"Separation of solid substances from their solution one by one depending upon their solubilities at different temperatures is called **fractional crystallization**."

A procedure for purifying the substance in which the impure solid is dissolved in a minimum amount of hot solvent. The solution is then gradually cooled, which cause crystals of pure substance to precipitate. These are collected by filtration while impurities remain in the solution.

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The solubility curve shows that solubility changes by variation of temperature.

For example, the change in solubility, in case of KNO_3, is very rapid with changing temperature, while such a change is more gradual in other cases like KBr, KCl. These differences in the behaviour of compounds provide the basis for fractional crystallization, which is a technique for the separation of impurities from the chemical products.

Method of Separation:

By using the method, the impure solute is dissolved in a hot solvent in which the desired solute is less soluble than impurities. As the hot solution is cooled, the desired solute being comparatively less soluble, separates out first from the mixture, leaving impurities behind in solution. In this way pure desired product crystallizes out from the solution.

COLLIGATE PROPERTIES OF SOLUTIONS

"The properties of solutions that depends upon the number of solute particles in given quantity of solvent but not on the nature of solute, are called **colligate properties**."

Colligate properties are given below:

(1) Lowering of the vapour pressure
(2) Elevation of boiling point (Ebullioscopy)
(3) Depression of freezing point (Cryoscopy)
(4) Osmotic pressure

First three properties are discussed here.

(a) LOWERING OF VAPOUR PRESSURE

The reason for these properties to be called colligate can be explained by considering three solutions. Let us take 6 g of urea, 18 g of glucose and 34.2 g of sucrose and dissolve them separately in 1 kg of H_2O. This will produce 0.1 molal solution of each substance. Pure H_2O has certain value of vapour pressure at a given temperature. In these three solutions, the vapour pressures will be lowered. The reason is that the molecules of a solute, present upon the surface of a solution decrease the evaporating capability. Apparently it seems that sucrose solution show the maximum lowering of vapour pressure while urea should have minimum lowering of vapour pressure. the reality is that the lowering of vapour pressure in all these solutions will be same at a given temperature. Actually the number of particles of the solute in all the solutions are equal. We have added $1/10^{th}$ of Avogadro's number of particles (6.02×10^{22}). The lowering of vapour pressure depends upon the number of solute particles and not upon their molar mass and structures. It should be kept in mind that these three **solutes are non-volatile and non-electrolyte**.

(b) ELEVATION OF B.P. AND DEPRESSION OF F.P.

The boiling points of these solutions are higher than that of pure solvent. It is observed that the boiling point elevation of these three solutions is 0.052^oC. Similarly freezing points will be depressed for these solutions and the value of depression in these three cases is 0.186^oC. The reason again is that the elevation of boiling point and the depression of freezing point depend upon number of particles of solute.

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Now let us deduce the values of elevation of the boiling point and the depression of the freezing point of water for 1 molal solutions. For that purpose, try to dissolve 60 g of urea, 180 g of glucose and 342 g of sugar separately of freezing point of water will be $0.52^{o}C$ and $1.86^{o}C$ respectively. All the three solutions will boil at $100.52^{o}C$ and freeze at $-1.86^{o}C$. These values of elevation of boiling point and depression of freezing are called **molal boiling point constant** and molal freezing point constant of H_2O denoted by K_b and K_f. These are also named as **ebullioscopic constant and cryoscopic constant** respectively. These constants depend upon the **nature of solvent and not upon the nature of solute**. Following table give the values of K_b and K_f for some common solvents.

TABLE

K_b and K_f Values for Some Solvents				
Solvent	**B.P. ^{o}C**	**K_b ($^{o}C/m$)**	**F.P. ^{o}C**	**K_f ($^{o}C/m$)**
H_2O	100	0.52	0	1.86
Ether	34.4	2.16	– 116.3	1.79
Acetic acid	118	3.07	17	3.90
Ethanol	79	1.75	– 114.5	1.99
Benzene	80	2.70	5.5	5.10

To observe the colligate properties, following condition should be fulfilled by the solutions.

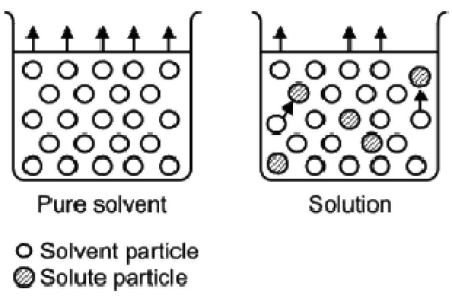
(a) Solution should be dilute.

(b) Solute should be non–volatile.

(c) Solute should be non–electrolyte.

1. LOWERING OF VAPOUR PRESSURE

In a pure solvent, particles can escape from all over the surface of the liquid. However, if some non–volatile, solute is added to the solvent, escaping tendency of the solvent decreases. In this way, vapour pressure of solution is less than the vapour pressure of pure solvent.



Non-voltaic solute particles inhibit solvent particles from escaping from the surface and thus lower vapour pressure

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A quantitative relationship between the change of vapour pressure of a solvent due to addition of non–volatile and non–electrolyte solute and the mole fraction of solute has been given by Raoult.

Relative lowering of vapour pressure is equal to the mole fraction of solute.

$$\frac{\Delta p}{p^o} = x_2$$

If n_2 and n_1 are the number of moles of a solute and solvent respectively, then

$$x_2 = \frac{n_2}{n_1 + n_2}$$

So, $$\frac{\Delta p}{p^o} = \frac{n_2}{n_1 + n_2}$$

For a dilute solution n_2 can be ignored in denominator because n_2 is very small.

Hence, $$\frac{\Delta p}{p^o} = \frac{n_2}{n_1}$$

The number of moles of solute and solvent are obtained by dividing their masses in grams with their respective relative molecular masses. If W_1 and W_2 are the masses of solvent and solute while M_1 and M_2 are their relative molecular masses respectively, then

$$n_1 = \frac{W_1}{M_1} \quad \text{and} \quad n_2 = \frac{W_2}{M_2}$$

$$\frac{\Delta p}{p^o} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}}$$

$$\frac{\Delta p}{p^o} = \frac{W_2}{M_2} \times \frac{M_1}{W_1} \qquad (1)$$

or $$M_2 = \frac{p^o}{\Delta p} \cdot \frac{W_2 M_1}{W_1} \qquad (2)$$

The molecular mass (M_2) of a non–volatile solute can be calculated from the equation.

Example 10:

Pure benzene has a vapour pressure of 122.0 torr at 32.^{o}C. When 20 g of a non–volatile solute were dissolved in 300 g of benzene, a vapour pressure of 120 torr was observed. Calculate the molecular mass of the solute the molecular mass of benzene being 78.1.

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Solution:

Let the molecular mass of the solute be = M_2

Mass of solute dissolved (W_2) = 20 g

Vapour pressure of pure solvent (p^o) = 122.0 torr

Vapour pressure of solution (p) = 120.0 torr

Lowering of vapour pressure (Δp) = 122.0 – 120.0
= 2.0 torr

Mass of solvent (W_1) = 300 g

Molar mass of solvent (M_1) = 78.1

Formula applied $\frac{\Delta p}{p^o} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$

$$M_2 = \frac{p^o}{\Delta p} \frac{W_2 M_1}{W_1}$$

Putting the values

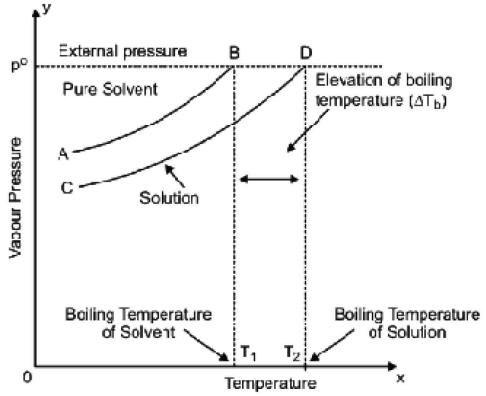
$$M_2 = \frac{122.0}{2.0} \times \frac{20 \times 78.1}{300}$$

$$M_2 = 317.6 \text{ g mol}^{-1}$$

2. ELEVATION OF BOILING POINT (EBULLIOSCOPY)

"Boiling point of a liquid depends upon the vapour pressure when some non–volatile and non–electrolyte solute is added to a solvent, the boiling point of solution increases called **elevation of boiling point**."

In order to understand it, determine the vapour pressure of a solvent at various temperatures. Plot a graph between temperature on x–axis and vapour pressures on y–axis. A rising curve is obtained with the increase of temperature. The slope of the curve at high temperature is greater, which shows that at high temperature, the vapour pressure increases more rapidly. Temperature T_1 on the curve AB which is for the pure solvent, corresponds to the boiling point of the solvent. The solvent boils when its vapour pressure becomes equal to the external pressure represented by p^o.



Elevation of boiling temperature curve

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When the solute is added in the solvent and vapour pressures are plotted vs temperatures, then a curve CD is obtained. This curve is lower than the curve AB because vapoure pressures of solution are less than those of pure solvent. Solution will boil at higher temperature T2 to equalize its pressure to p^o. The difference of two boiling points give the elevation of the boiling point ΔT_b.

The higher the concentration of solute, the greater will be the lowering in vapour pressure of solution and hence higher will be its boiling point. So elevation of boiling point ΔT_b is directly proportional to the molality of solution.

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b\, m \qquad (1)$$

Where K_b is called **the ebullioscopic constant or molal boiling point constant**.

$$\Delta T_b = T_2 - T_1$$

Molal boiling point constant or Ebullioscopic constant (K_b):

"The elevation in boiling point when 1 mole of solute is dissolved to the one kilogram of solvent is called **molal boiling point constant or ebullioscopy constant**."

$$\Delta T_b = K_b\, m$$

When m = 1, $\Delta T_b = K_b$

The unit of K_b is $^oC\ kg\ mol^{-}$

Equimolar solution of different non–electrolytes **increase the boiling point equally**. For example, 6 g of Urea 18 g of glucose and 34.2 g of $C_{12}H_{22}O_{11}$ when dissolved in 1 kg of solvent, increases the boiling point equally because, the molality is same.

We know that

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1000}{\text{Mass of solvent in grams}}$$

or $$m = \frac{W_2}{M_2} \times \frac{1000}{W_1} \qquad (2)$$

Where W_1 = mass of solvent in grams

W_2 = mass of solute

M_2 = molar mass of solute

Put the value of Equation (2) in Equation (1).

$$\Delta T_b = K_b \frac{W_2\ 1000}{M_2 \times W_1}$$

By rearranging we get

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1} \times 1000 \qquad (3)$$

This Equation (3) can be used to determine the molar mass of non–electrolyte solute.

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MEASUREMENT OF BOILING POINT ELEVATION (LANDSBERGER'S METHOD)

This is one of the best methods for the measurement of boiling elevation of a solution. The apparatus consists of four major parts.

(a) An inner tube with a hole in its side. This tube is graduated.

(b) A boiling flask which sends the solvent vapours into the gradual tube through a rose head.

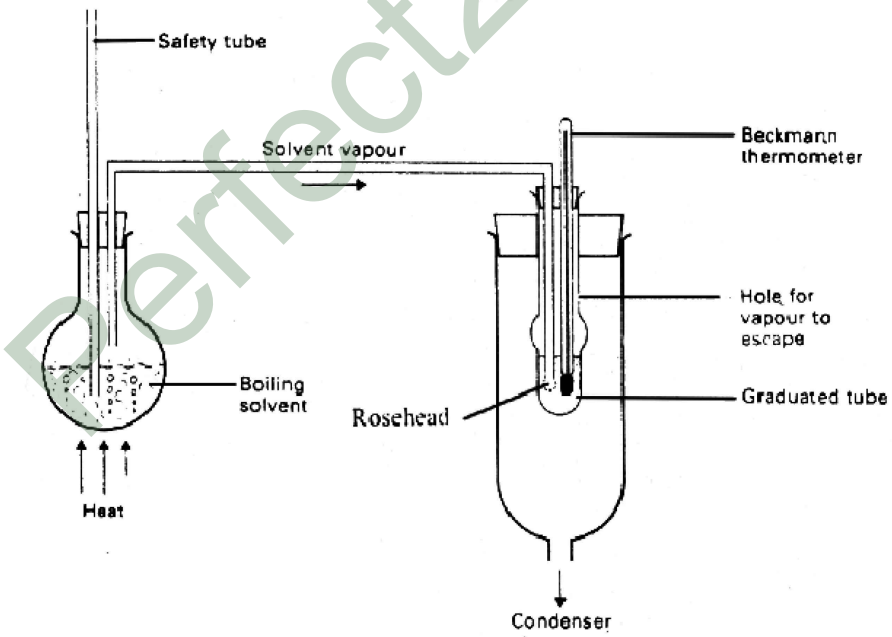
(c) An outer tube, which receives hot solvent vapours coming from side hole of the inner tube.

(d) A thermometer which can read up to 0.01 K.

The solvent is placed in the inner tube. Some solvent is also taken separate flask and its vapour are sent into this tube. These vapours cause the solvent in the tube to boil by its **latent heat of condensation**. This temperature is the boiling point of the pure solvent.

The supply of the vapours is temporarily cut off and a weighed pellet of solute is dropped in the inner tube. The vapours of the solvent are again pass through it until the solution is boiled. This temperature is again noted.

Now the supply of the solvent vapours is cut off, the thermometer and the rose head are removed and the volume of the solution is measured. The difference of the two boiling points gives the value ΔT_b. The following formula is used to calculated the molecular mass of solute.



$$M_2 = \frac{K_b}{\Delta T_b} \frac{1000\ W_2}{W_1} \qquad (1)$$

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Latent Heat of Condensation:

"The amount of heat evolved when one mole of vapours are condensed to a liquid at constant temperature is called **latent heat of condensation**."

It is an exothermic process

Vapour $\longrightarrow$ Liquid $\quad \Delta H = -$ heat

Example 11:

The boiling point of water is 99.725°C. To a sample of 600 g of water are added 24.0 g of a solute having molecular mass of 58 g mol^{-1} to form a solution. Calculate the boiling point of the solution.

($K_b = 0.52°C\ kg\ mol^{-1}$)

Solution:

Boiling point of pure $H_2O = 99.725°C$

Mass of solvent $(H_2O)\ W_1 = 600\ g$

Mass of solute $(W_2) = 24.00\ g$

Molar mass of solute $(M_2) = 58\ g\ mol^{-1}$

The molar boiling point constant of $H_2O\ (K_b) = 0.52°C\ kg\ mol^{-1}$

$$\Delta T_b = K_b \times \frac{1000\ W_2}{W_1 \times M_2}$$

$$= \frac{0.52 \times 1000 \times 24.00}{600 \times 58} = 0.358°C$$

Boiling point of solution = boiling point of pure solvent + elevation of boiling point

$= 99.725 + 0.358$

$= 100.083°C$

3. DEPRESSION IN FREEZING POINT (CRYOSCOPY)

The **freezing point** of a substance is the temperature at which the solid and liquid phases of the substance co–exist.

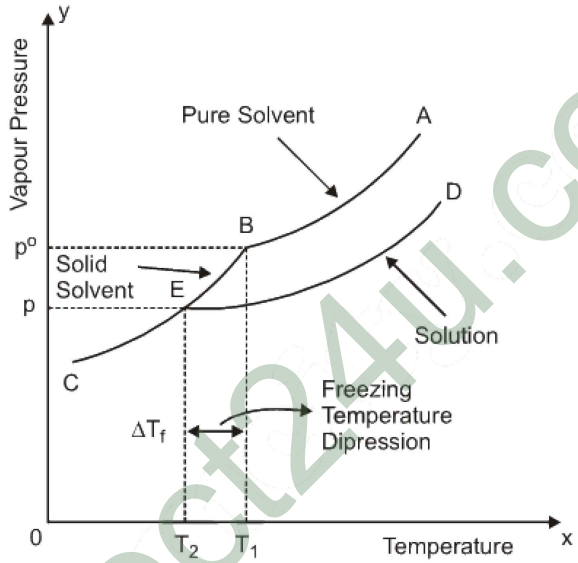
Freezing point is also defined as that temperature at which its solid and liquid phases have the **same vapour pressures**.

When a non–volatile solute is added to a solvent, its vapour pressure is decreased. At the freeing point there are liquid solution and the solid solvent in the vessel. The **solution will freeze** at that temperature at which the **vapour pressures of both liquid solution and solid solvent are same**. It means that a solution should freeze at lower temperature than the pure solvent.

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In order to understand it, plot a graph between vapour pressure and T_1 temperature of pure solvent and that of solution. The curve ABC is for the pure solvent. The solvent freezes at temperature T_1 corresponding to the point B when the vapour pressure of freezing solvent is p^o. The portion of the curve BC is for the solid solvent. This portion has a greater slope showing that the change of vapour pressure with the change of temperature is more rapid.

The curve DEC for the solution will meet the curve BC at the point E. This is the freezing point of solution T_2 and corresponds to the vapour pressure p which is lower than p^o. The reason is that vapour pressure of solution is less than the pure solvent.



Depression of freezing point curve

Depression of freezing point = freezing point of pure solvent – freezing point of solution

So $\Delta T_f = T_1 - T_2$

This depression of freezing point ΔT_f when a solute is added to a solvent is related to the molality (m) of the solution. The relationship is similar to that of elevation of the boiling point.

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m \qquad (1)$$

K_f is called the **molal freezing point constant** or the cryoscopic constant and m is the molality of the solution.

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1000}{\text{Mass of solvent gram}}$$

or $$m = \frac{W_2}{M_2} \times \frac{1000}{W_1}$$

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Where W_2 = mass of solute in grams

W_1 = mass of solvent

and M_2 = molar mass of solute

Put the value of this molality in Equation (1).

$$\Delta T_f = K_f \frac{1000\ W_2}{M_2 \times W_1}$$

$$\text{Molar mass of solute } (M_2) = \frac{K_f}{\Delta T_f} \frac{1000\ W_2}{W_1} \qquad (2)$$

Molal Freezing Point Constant or Cryoscopic Constant (K_f):

"The depression in freezing point when one mole of solute is dissolved to one kilogram of solvent is called **cryoscopic constant or molal freezing point constant**."

$$\Delta T_f = K_f\, m$$

when $m = 1$, $\Delta T_f = K_f$

Units:

$$K_f = \frac{\Delta T_f}{m} = \frac{^oC}{\text{mol kg}^{-1}} = {}^oC\ \text{kg mol}^{-1}$$

MEASUREMENT OF FREEZING POINT DEPRESSION (BECKMAN'S FREEZING POINT APPARATUS)

There are many methods but Beckman's method is easy to perform.

The apparatus consists of three major parts.

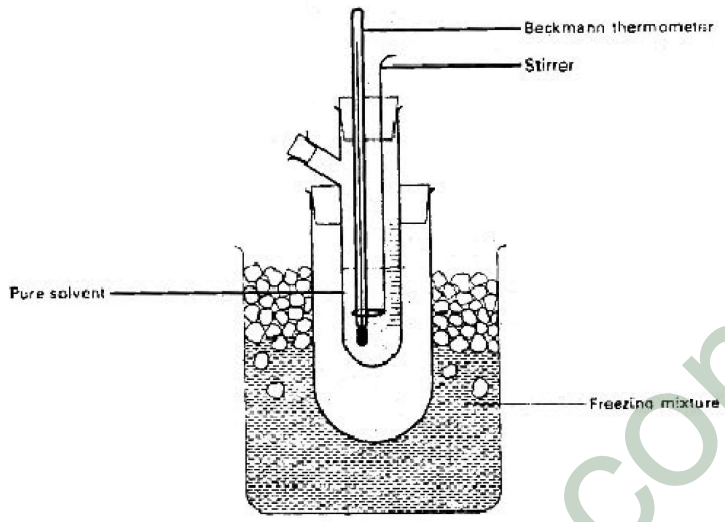
(a) **A freezing tube with a side arm**. It contains solvent or solution and is fitted with a stirrer and a Beckman thermometer.

(b) **An outer larger tube** into which the freezing tube is adjusted. The air jacket in between these tubes help to achieve a slower and more uniform rate of cooling.

(c) **A larger jar containing a freezing mixture**.

Around 20 to 25 g of the solvent is taken in the freezing tube. The bulb of the thermometer is immersed in the solvent. First of all approximate freezing point of the solvent is measured by directly cooling the freezing point tube in the freezing mixture.

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Apparatus for determining depression of freezing point

The freezing tube is then put in the air jacket and cooled slowly. In this way accurate freezing point of the solvent is determined. Now the solvent is re–melted by removing the tube from the bath and weighed amount (0.2 to 0.3 g) of the solute is introduced in the side tube. The freezing point of the solution is determined while stirring the solution. The difference of the two freezing points gives the value of ΔT_f and the following formula is used to calculate the molar mass of solute.

$$M_2 = \frac{K_f}{\Delta T_f} \frac{1000\ W_2}{W_1}$$

Example 12:

The freezing point of pure camphor is 178.4°C. Find the freezing point of a solution containing 2.0 g of a non–volatile compound, having molecular mass 140, in 40 g of camphor. The molal freezing point constant of camphor 37.7°C kg mol¯1.

Solution:

Freezing point of camphor = 178.4°C

Mass of solute (W_2) = 2.00 g

Mass of solvent (W_1) = 40 g

Molar mass of solute (M_2) = 140 g mol^{-1}

The molal freezing point constant of solvent = 37.7°C kg mol^{-1}

Freezing point of solution = ?

Applying the equation $\Delta T_f = K_f \frac{1000\ W_2}{W_1 \times M_2}$

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We have to calculate the freezing point of solution, so first we get the depression in freezing point ΔT_f then subtract it from freezing point pure solvent.

$$\Delta T_f = \frac{37.7 \times 1000 \times 2}{40 \times 140} = 13.46^oC$$

Freezing point of solution = 178.4 – 13.46 = 164.94^oC

APPLICATION OF BOILING POINT ELEVATION AND FREEZING POINT DEPRESSION PHENOMENA

(1) These phenomena are used to determine the molecular masses of the compounds.

(2) This phenomenon find use as antifreeze in the radiator of an automobile. In radiators of automobiles, ethylene glycol ($C_2H_6O_2$) is added. It is completely miscible in water but have very low vapour pressure because it is non–volatile. When mixed with water, it lowers the freezing point as well as raises the boiling point. During winter it protects a car by preventing the liquid in the radiator from freezing, as water alone. In hot summer the antifreeze solution also protects the radiator from boiling over.

(3) Another common application is the use of NaCl or KNO_3 to lower the melting point of ice. One can prepare freezing mixture for use in an ice cream machine.

(4) In some countries NaCl is sprayed over roads for de–icing of road.

ENERGETIC OF SOLUTIONS

The heat of solution of a substance depends upon the relative magnitude of two processes.

First Process:

When a solid is dissolved in a liquid, a **change in the physical state** of liquid takes place. **Energy is absorbed** in overcoming the intrinsic or intermolecular forces, that holds the particles of substance in their crystal lattices. On the other hand the distance between solute and solvent molecules or ions increases, as compared to their pure state. This increase in distance of solvent molecule also required energy. It is also an **endothermic** process and change is physical change.

Second Process:

In second process a **chemical reaction** between solute molecule or ion and solvent molecule takes place. New forces are established between the solute and solvent molecules. The second change is **usually an exothermic process**.

If heat evolved in chemical change is greater than that absorbed in the physical change the heat of solution is negative and net process is exothermic. If heat evolved in chemical change is lesser than that absorbed in the physical change, the heat of solution is positive and net process is endothermic.

"The quantity of heat absorbed or evolved when one mole of a substance is dissolved in specific amount of solvent at given temperature, is called **heat of solution**."

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When **potassium nitrate** is dissolved in water, the temperature of the solution decreases indicating an **endothermic process**, while solution of **lithium chloride** in water produces heat, showing that the process of dissolution is **exothermic**. The quantity of heat energy, that is absorbed or released when a substance forms solution, is termed as heat of solution.

It is given the symbol $\Delta H_{(sol)}$. The $\Delta H_{(sol)}$ gives the difference between the energy possessed by the solution after its formation and the original energy of the components before their mixing i.e.

$$\Delta H_{(sol)} = H_{solution} - H_{components}$$

Here $H_{(sol)}$ is the energy content of solution **after its formation** while $H_{components}$ represents the energy contents of components **before their mixing**. However, both these factors cannot actually be measured, only their difference i.e., the change $\Delta H_{(sol)}$ is practically measurable. If the value of $\Delta H_{(sol)}$ is negative, it would mean that the solution is having less energy than the components from which it was made, hence the dissolution process is an exothermic one. On the other hand an endothermic process would have a positive $\Delta H_{(sol)}$ value.

TABLE

Heats of Solution of Some Ionic Solids at Infinite Dilution

Substance	**Heat of Solution ($kJ\ mol^{-1}$ of solute)**	**Substance**	**Heat of Solution ($kJ\ mol^{-1}$ of solute)**
NaCl	4.98	NH_4Cl	16.0
NH_4NO_3	26.0	LiCl	– 37.0
KCl	17.2	$AlCl_3$	– 321.0
KI	20.3		

The magnitude of heat of solution gives **information** regarding the **strength of intermolecular forces of attraction** between components which mix to form a solution.

When one mole (58.5 g) of sodium chloride is dissolved in 10 moles (180 g) of water 2.008 kJ of energy is absorbed.

$$NaCl + 10H_2O \longrightarrow NaCl\,(10H_2O) \quad \Delta H = +2.008\ kJ$$

On diluting a concentrated solution there is a further heat change. This heat change depends on the amount of water used for dilution. The heat of dilution gradually decreases, so that eventually increasing the dilution produces no further heat change. This occurs when there are 800 – 1000 moles of water to one mole of solute. This stage is called **infinite dilution** and the heat of solution is expressed as:

$$NaCl_{(s)} + Water \longrightarrow NaCl_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)} \quad \Delta H = +4.98\ kJ\ mol^{-1}$$

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HYDRATION AND HYDROLYSIS

Hydration:

"The process in which water molecules surround and interact with solute particles is called **hydration**."

Salvation:

"The process in which solvent molecules surround and interact with solute particles is called **salvation**."

When ionic compounds are dissolved in water, they are dissociated into ions. Negative ions are surrounded by water molecules. The partial positively charged hydrogen atoms of water surround and attract the anions with electrostatic forces of attraction. Similarly, positive ions of solute, create attractions with partial negative oxygen atoms of water molecules. In this way, all the ions in the aqueous solution are hydrated.

The ions, which are surrounded by water molecules, are called **hydrated ions**. The number of water molecules which surround a given ion depends upon the size of the ions and the magnitude of its charge. If the size of the ion is small and is highly charged positive ion then greater number of water molecules will surround it. negatively charged ions have smaller number of water molecules surrounding them. Hence the ions with high **charge density** (charge/unit area) has a greater ability to attract polar water molecules than ions with smaller charge density.

Hydrates:

"The crystalline substances which have water of crystallization in them are called **hydrates**."

In hydrates, mostly water molecules are attached with cations rather than anions due to their greater charge density. Formation of hydrates takes place in salts, acids, bases and some elements.

When aqueous solution of many soluble salts are evaporated the salt separates as crystals that contain the salt and water combined in a definite proportion.

For example, copper sulphate is penta hydrated $CuSO_4\ 5H_2O$. Four water molecules are attached with Cu^{2+} and one molecule with SO_4^{2-} Cu^{2+} has greater charge density than anion. Some other examples of hydrates are given below:

$(COOH)_2 . 2H_2O$	$BaCl_2 . 2H_2O$	$Na_2CO_3 . 10H_2O$
$MgCl_2 . 6H_2O$	$Na_2B_4O_7 . 10H_2O$	$CaSO_4 . 2H_2O$
$MgSO_4 . 7H_2O$	$AlCl_3 . 6H_2O$	$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$
$FeSO_4 . 7H_2O$	$FeSO_4 . (NH_4)_2SO_4 . 6H_2O$	$(NH_4)_2C_2O_4 . H_2O$

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Energies of Hydrations:

When a crystal is added to a solvent, the solvent molecules start attaching themselves to the lattice. Some interaction usually takes place between liquid and solid releasing energy of salvation which causes the affected crystal particles to oscillate vigorously and break from the lattice. The energy of salvation must exceed the energy used to disrupt the lattice and separates its constituent particles. This process will continue all over the surface of the crystal. When potassium iodide (KI) is added to water hydration takes place in two steps.

1. Separation of Ions:

The first step breaks the lattice to separate the ions. Since energy is required to accomplish this step, so this step is **endothermic**. The amount of energy needed to separate a crystalline compound into isolated ions (or atoms) is known as **lattice energy**. The lattice energy of ionic solids is always higher than molecular solids.

$$KI_{(s)} \longrightarrow K^+_{(g)} + I^-_{(g)}$$

2. Hydration Energy of Ions:

In the second step, the ions are brought into water and get hydrated (solvated). A hydrated ions is attracted by the solvent dipoles and energy is released, so this step is exothermic. The energy given out by this step is known as the hydration energy (or salvation energy).

$$K^+_{(g)} + I^-_{(g)} + H_2O \longrightarrow K^+_{(aq)} + I^-_{(aq)}$$

The overall change that takes place when KI dissolves in water can be represented as:

1st Step:

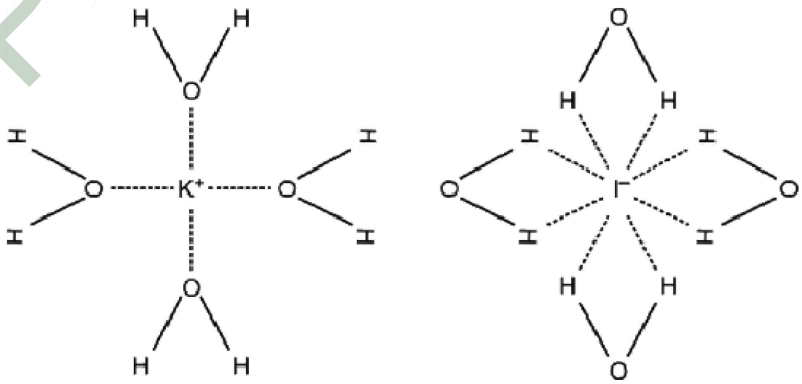
$$KI_{(s)} \longrightarrow K^+_{(g)} + I^-_{(g)}$$

2nd Step:

$$K^+_{(g)} + I^-_{(g)} + H_2O \longrightarrow K^+_{(aq)} + I^-_{(aq)}$$

$$KI_{(s)} + H_2O \longrightarrow K^+_{(aq)} + I^-_{(aq)}$$

The values of hydration energies of individual ions i.e. cations and anions are given in Table. It is interesting to compare these values with the ionic radii of the ions. Greater the size of monovalent cation lesser is the heat of hydration. Divalent and trivalent cations have higher values due to high charge densities. Anions also show definite trend of heat of hydration.



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TABLE

Hydration Energies of Common Ions					
Ion	**kJ mol^{-1}**	**Ion**	**kJ mol^{-1}**	**Ion**	**kJ mol^{-1}**
H^+	– 1075	K^+	– 305	F^-	– 457
Li^+	– 499	Mg^+	– 1891	Cl^-	– 384
Na^+	– 390	Cu^+	– 1562	Br^-	– 351
Ag^+	– 464	NH_4^+	– 281	OH^-	– 460
		Al^{+++}	– 4613		

Hydrolysis of Salt:

"Some cations or anions of salts reacts with water and form acidic or basic solution respectively, is called **hydrolysis**."

The concentration of each of H^+ and OH^- ions are equal to 10^{-7} M, as in pure water. But this balance between H^+ and OH^- ions can be disturbed with resulting change in the pH of solution when other salts are dissolved in water.

For example;

(1) NaCl is dissolved in water, no change in pH takes place.

(2) Na_2CO_3 is dissolved in water, solution becomes basic and pH of solution is greater than 7.

(3) $CuSO_4$ is dissolved in water, solution becomes acidic and pH of solution is less than 7.

There are some cations or anions which undergoes chemical reactions with water (hydrolytic reaction) and concentration of H^+ and OH^- becomes unbalanced in water.

Cations which undergo hydrolysis:

Usually cations of large size undergo hydrolysis e.g. Cu^{2+}, Zn^{2+} Al^{3+}, NH_4^+, etc.

Anions which undergo hydrolysis:

Conjugates bases of weak acids, undergo hydrolysis. These are weak bases and reacts with water to produce OH^- ions.

$$CH_3COO^- + HOH \longrightarrow CH_3COOH + OH^-$$

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Example:

CH_3COO^-, CN^-, $C_2O_4^{2-}$, S^{2-}, HCO_3^{-1}, CO_3^{-2}

1. Hydrolysis of salt of strong acids with strong bases:

Such salts do not hydrolysis in water and pH of water remain unchanged. For example, NaCl, KCl, K_2SO_4, Na_2SO_4, KBr, NaBr, NaI, etc.

The positive ions Na^+, K^+, are not hydrolyzed in water. Similarly, Cl^-, Br^-, SO_4^{2-}, I^- are also not hydrolyzed by water.

2. Hydrolysis of salt of strong acids with weak bases:

Such salts when dissolved in water, they produces strong acids and weak bases. Due to greater ionization of acids, they have higher value of Ka. The solution will be acidic and pH of solution will be less than 7 e.g.

$$AlCl_3 + H_2O \longrightarrow Al(OH)_3 + 3H^+ + 3Cl^-$$

$$NH_4Cl + H_2O \longrightarrow NH_4OH + H^+ + Cl^-$$

$$CuSO_4 + 2H_2O \longrightarrow Cu(OH)_2 + 2H^+ + SO_4^{2-}$$

3. Hydrolysis of salt of weak acids with strong bases:

Salt of weak acids with strong basis on hydrolysis produce basic solution and pH of solution is greater than 7. Such salts form strong bases by reacting with water e.g.

$$CH_3COONa + H_2O \longrightarrow CH_3COOH + Na^+ + OH^-$$

$$Na_2S + 2H_2O \longrightarrow H_2S + 2Na^+ + 2OH^-$$

$$NaHCO_3 + H_2O \longrightarrow H_2CO_3 + Na^+ + OH^-$$

$$Na_2CO_3 + 2H_2O \longrightarrow H_2CO_3 + 2Na^+ + 2OH^-$$

$$Na_3PO_4 + 3H_2O \longrightarrow H_3PO_4 + 3Na^+ + 3OH^-$$

4. Hydrolysis of salt of weak acids with weak bases:

Salt of weak acids with bases also undergo hydrolysis. Acidic or basic nature depends upon the values of K_a and K_b respectively e.g.

$$CH_3COO\,NH_4 + H_2O \longrightarrow NH_4OH + CH_3COOH$$

If $K_a = K_b$ solution will be neutral.

If $K_a > K_b$ solution will be acidic.

If $K_a < K_b$ solution will be basic.

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EXERCISE

Q.1 Chose the correct answer for the given ones:

(i) Molarity of pure water is:

(a) 1 (b) 18

(c) 55.5 (d) 6

(ii) 18 g glucose is dissolved in 90 g of water. The relative lowering of vapour pressure is equal to:

(a) $\frac{1}{5}$ (b) 5.1

(c) $\frac{1}{51}$ (d) 6

(iii) A solution of glucose is 10 percent. The volume in which 1 g mole of it is dissolved will be:

(a) 1 dm^3 (b) 1.8 dm^3

(c) 200 Cm^3 (d) 900 Cm^3

(iv) An aqueous solution of ethanol in water may have vapour pressure:

(a) Equal to that of water (b) Equal to that of ethanol

(c) More than that of water (d) Less than that of water

(v) An azeotropic mixture of two liquids boils at a lower temperature than either of them when:

(a) It is saturated

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

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

(d) It is metastable.

(vi) An azeotropic mixture showing positive deviation from Raoult's law, the volume of the mixture is:

(a) Slightly more than the total volume of the components

(b) Slightly less than the total volume of the components

(c) Equal to the total volume of the components

(d) None of these

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(vii) Which of the following solutions has the highest boiling point:

(a) 5.85 percent solution of sodium chloride

(b) 18.0 percent solution of glucose

(c) 6.0 percent solution of urea

(d) All have the same boiling point

(viii) Two solutions of NaCl and KCl are prepared separately by dissolving same amount of the solute in water. Which of the following statements is true for these solutions:

(a) KC1 solution will have higher boiling point than NaCl solution

(b) Both of the solutions have different boiling points

(c) KC1 and NaCl solution possess same vapour pressure

(d) KCl solution possesses lower freezing point than NaCl solution

(ix) The molal boiling constant is the ratio of the elevation in boiling point to:

(a) Molarity (b) Molality

(c) Mole fraction of solvent (d) Mole fraction of solute

(x) Colligative properties are the properties of:

(a) Dilute solution which behave as nearly ideal solutions

(b) Concentrated solutions which behave as nearly non-ideal solutions

(c) Both (a) and (b)

(d) Neither (a) nor (b)

ANSWERS

Answers	Reasons
(i) (c)	Molarity is the number of moles per litre (1 dm^3). And density of water is g/cm^3 1 g = 1 cm^3 1000 g = 1000 cm^3 = 1 dm^3 The mass of 1 dm^3 is 1000 g. We can calculate the no. of moles in 1000 g (1 dm^3) of pure water $n = \frac{m}{M} = \frac{1000}{18} = 55.5$ moles

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(ii) (b) The relative lowering of vapour pressure is equal to mole fraction of solute

$$\frac{\Delta P}{P^o} = x_2$$

Mole fraction of solute (x_2) can be calculated by knowing the no. of moles of solute and solvent. No. of moles of glucose in 18 g $= \frac{18}{180} = \frac{1}{10} = 0.1$ moles.

No. of moles of water in 90 g $= \frac{90}{18} = 5$ moles. Hence, mole fraction of solute (x_2) is the ratio of no. of moles of solute to the total no. of moles

$$x_2 = \frac{0.1}{0.1 + 5} = \frac{0.1}{5.1} = \frac{1}{51}$$

and $\boxed{\frac{\Delta P}{P^o} = \frac{1}{51}}$

(iii) (b) 10% w/v glucose solution means

10 g of glucose = 100 cm^3 of solution

1 g of glucose = $\frac{100}{10}$ cm^3 of solution

and 180 g (1 g mole) of glucose = $\frac{100}{10} \times 180$ cm^3 of solution

= 1800 cm^3

= 1.8 dm^3 of solution

(1 dm^3 = 1000 cm^3)

Hence, the volume of solution in which 1 g mole (180 g) of glucose is present is 1800 cm^3 (1.8 dm^3)

(iv) (c) The solution ethanol in water shows positive deviation from Raoult's Law. It means that vapour pressure of solution is greater and boiling point is lesser than either of the two component.

Boiling point of water = 100°C

Boiling point of ethanol = 78.5°C

Boiling point of solution = 78.1°C

(v) (b) An azeotropic mixture of two liquids that boils at lower temperature than either of them, then its vapour pressure is higher than either of them. And a solution whose vapour pressure is greater than either of two components.

(vi) (a) When azeotropic mixture shows positive deviation from Raoult's law, then its vapour pressure is greater than either of the two components. Increase of vapour pressure is only possible when there is decrease of intermolecular force between solute and solvent molecules. The decrease of forces leads to increase of volume of two components.

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(vii)	(a)	5.85% NaCl solution means 5.85 g (0.1 mole) of NaCl in 100 g of solution. 18.0% glucose solution means 1.8 g (0.1 mole) of glucose in 100 g of solution. 6.0% urea solution means 6 g (0.1 mole) of urea 100 g of solution. All the solutions contains 0.1 moles of respective species per 100 g of solution. 0.1 moles of both glucose and urea produces 6.02×10^{23} particles in solution whereas 0.1 moles of NaCl produces $2 \times 6.02 \times 10^{23}$ particles in solution because NaCl ionizes and produces twice the no. of ions than formula. Unit 5.85% NaCl solution will have highest boiling point than other two species because it contain twice no. of particles than other two.
(viii)	(b)	The molar mass of NaCl is 5.85 g/mole and that of KCl is 74.5 g/mole. 1 formula unit of both the species produces two ions in the solution. If we consider the same amount (mass) i.e., 58.5 g of both the species, then 58.5 g of NaCl (equal to its 1 mole) produces twice the Avogadro's number of particles (ions). Whereas 58.5 g KCl (less than its one mole) produce less than twice the N_A of ions. Hence, the 58.5 g of NaCl solution containing greater number of particles (ions) have higher boiling point than KCl solution. In other words, both have different boiling point. Note: (For this case only) 1. The boiling point of NaCl solution is higher and its freezing point is lesser than KCl solution. 2. The vapour pressure of NaCl solution is lower than KCl solution.
(ix)	(b)	The boiling point elevation of a solution is directly proportional to molality of the solution. $\Delta T_b \propto m$ $\Delta T_b = K_b m$ $\boxed{K_b = \frac{\Delta T_b}{m}}$ Hence, molal boiling point constant is the ratio of boiling point elevation to molality of the solution.
(x)	(a)	Dilute solutions are usually ideal. Colligative properties are the properties of dilute solutions. For concentrated solutions, there are large numbers of solute particles very close to each other. Due to which attraction starts and particles associate. As a result, no. of particles reduces and effect on the property is also less. Hence concentrated solution do not behave ideally.

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Q.2 Fill in the blanks with suitable words:

(i) Number of molecules of sugar in 1 dm^3 of 1 M sugar solution is ————.

(ii) 100 g of a 10% aqueous solution of NaOH contains 10 g of NaOH in ———— g of water.

(iii) When an azeotropic mixture is distilled, it ———— remains constant.

(iv) The molal freezing point constant is also known as ———— constant.

(v) The boiling point of an azeotropic solution of two liquids is lower than either of them because the solution show ———— from Raoult's law.

(vi) Among equimolal aqueous solutions of NaCl, $BaC1_2$ and $FeC1_3$, the maximum depression in freezing point is shown by ———— solution.

(vii) A solution of ethanol in water shows ———— deviation and show azeotropic solution with ———— boiling point than other components.

(viii) Colligative properties are used to calculate ———— of compound.

(ix) The hydration energy of Br^- ion is ———— than that of F^- ion.

(x) The aqueous solution of NH_4Cl is ———— while that of Na_2SO_4 is ————.

ANSWERS

Answers		Explanation
(i)	6.02×10^{23}	1 dm^3 of 1M sugar solution contains 1 mole of sugar. And there 6.02×10^{23} molecules of sugar in the solution.
(ii)	90 g	10% NaOH solution means 10 g of NaOH and 90 g of water to make total 100 g of solution.
(iii)	Composition	Azeotropic mixture (corresponding to specific composition distil without change in composition and have constant boiling point.
(iv)	Cryoscopic	
(v)	Positive deviation	When Azeotropic solution have boiling point less than either of the component, then its vapour pressure will be higher than either of two components and is said to show positive deviation from Raoult's law.
(vi)	$FeCl_3$	Freezing point depression is a colligative property and depends upon number of solute particles. 1 molal solution of NaCl have twice the Avogadro's no. of ions, and 1 molal solution of $BaCl_2$ have thrice the Avogadro's no. of ions and 1 molal solution of $FeCl_3$ have, four times the Avogadro's no. of ions when dissolved in water. Amongst the equimotal. (1 molal) solutions of all the three species, $FeCl_3$ produced greatest no. of ions in the solution. Hence, it has maximum depression in freezing point.

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(vii)	Less	Ethanol solution in water shows positive deviation i.e., have higher vapour pressure and low boiling point than component.
(viii)	Molar mass	Mathematical form at the end of each colligative property gives us basis for molar mass calculation of unknown compound e.g., mathematical equation for lowering of vapour pressure. $\frac{\Delta P}{P^\circ} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$ $\boxed{M_2 = \frac{P^\circ}{\Delta P} \times \frac{W_2}{W_1} M_1}$ M_2 is a molar mass of unknown compound.
(ix)	Lesser	The value of hydration energy depends upon charge to size ratio or charge density of ions. Greater the charge density, greater will be the Hydration energy. The charge on Br^- and F^- ion is same but the size of Br^- ion larger. Hence, Br^- ion will have low charge density and less hydration energy.
(x)	Acidic, neutral	NH_4Cl undergo hydrolytic reaction as $NH_4Cl + H_2O \longrightarrow NH_4OH + H^+ + Cl^-$ This produces weak base NH_4OH and Cl^- ion which is not hydrolysed. As a result H^+ ions are set free and solution becomes acidic. Na_2SO_4 ionizes as: $Na_2SO_4 + H_2O \rightleftharpoons 2Na^+ + SO_4^{2-} + H^+ + OH^-$ Na^+ ion and SO_4^{2-} are not hydrolysed by water. As a result, H^+ ion and OH^- concentration remains same and solution remains neutral.

Q.3 Indicate True or False from the given statement:

(i) At a definite temperature the amount of solute in a given saturated solution is fixed.

(ii) Polar solvents readily dissolve non-polar covalent compounds.

(iii) The solubility of substance decreases with increases in temperature if the heat of solution in negative.

(iv) The rate of evaporation of liquid is inversely proportional to the intermolecular forces of attraction.

(v) The molecular mass of an electrolyte determined by lowering of vapour pressure is less than the theoretical molecular mass.

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(vi) Boiling point elevation is directly proportional to the molality of the solution and inversely proportional to boiling point of solvent.

(vii) All solutions containing 1 g of non-volatile non-electrolyte solutes in same solvent will have same freezing point.

(viii) The freezing point of a 0.05 molal solution of a non-volatile non-electrolyte solute in water is $-0.93^{\circ}C$.

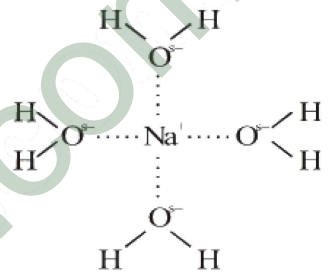
(ix) Hydration and hydrolysis are different process for Na_2SO_4.

(x) The hydration energy of an ion only depends upon its charge.

ANSWERS

Answers		Explanation
(i)	True	
(ii)	False	Polar solvents readily dissolve polar covalent compounds. The principle of dissolution is, like dissolve like i.e. Polar compounds are soluble is polar solvents whereas non-polar compounds are soluble in non-polar solvents. e.g., Sugar is soluble in water and I_2 is soluble in CCl_4.
(iii)	True	If the dissolution of a compounds is exothermic (heat of solution is negative), then rise of temperature will favour its crystallization which is endothermic. Hence, solubility decreases.
(iv)	True	If intermolecular forces of attraction between the molecules of liquid are stronger, then there are less chances for the molecules to escape from the surface. Hence, evaporation and intermolecular forces are inversely proportional.
(v)	True	
(vi)	False	Boiling points elevation is directly proportional to molality of the solution and is independent of boiling point of solvent. $\boxed{\Delta T_b \propto m}$ In this relationship, boiling point elevation has no relation with the boiling point of solvent.
(vii)	False	All the solutions containing 1 g of non-volatile, non-electrolyte solutes in same solvent will have different freezing point. 1g of all the electrolytes have different number of moles and molecules, since their molar masses are different. For example: 1 g of glucose will have moles $= \frac{1}{180}$ and 1 g of sucrose will have moles $= \frac{1}{342}$ Hence their no. of molecules will be different and freezing points also be different because it depends upon no. of solute particles.

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(viii)	False	The freezing point of a 0.05 molal solution of a non-volatile and non-electrolyte solute in water is −0.093°C. The molal freezing point of non-electrolyte solute in water is −1.86°C. Mean: Freezing point of 1 molal solution = −1.86°C Freezing point of 0.1 molal solution = −0.186°C Freezing point of 0.05 $\left(\frac{0.1}{2}\right)$ molal solution = $\left(-\frac{0.186}{2}\right)$ = −0.093°C
(ix)	True	Hydration is the surrounding of ions by water molecules with their oppositely charged ends whereas hydrolysis is the interaction of salt and water as a result of which salt dissociates in ions. $Na_2SO_4 \xrightleftharpoons{H_2O} 2Na^+ + SO_4^{-2}$ 
(x)	False	Hydration energy of an ion depends upon charge / size ratio (charge density) of ions. Greater the charge density of ion, greater will be its hydration energy.

Q.4 Define and explain the following with examples:

(a) A homogeneous phase (b) A concentrated solution

(c) A solution of solid in a solid (d) A consulate temperature

(e) A non-ideal solution (f) Zeotropic solution

(g) Heat of hydration (h) Water of crystallization

(i) Azeotropic solution (j) Conjugate solution

Ans.

(a) **A Homogeneous Phase:** A mixture of two or more substances with uniform composition and properties throughout the sample is called homogeneous phase.

Example: Sugar solution.

Note: If small amount of sugar is added to water, sugar is dissolved and the whole mixture is in liquid state with sweet taste. These properties remain uniform throughout the sample. Hence, sugar solution is said to be homogeneous phase.

(b) **A Concentrated Solution:** A solution containing relatively large amount of solute dissolved in solvent is called concentrated solution.

Example: 1 dm solution containing 50 g dissolved sugar is concentrated than 1 dm^3 solution containing 20 g dissolved sugar.

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(c) **A Solution of Solid in Solid:** A solution in which both solute and solvent are in solid phase is called solution of solid in solid.
Example: Metal alloys (homogeneous mixture of two or more metals).

(d) **A Consulate Temperature:** The temperature at which two conjugate solutions completely merge into each other is called consulate temperature or upper consulate temperature. It is also called critical solution temperature. OR
The temperature at which two polarity miscible liquids forms homogeneous mixture (a true solution) is called consulate temperature.
Example: The consulate temperature for phenol-water system is 65.9°C.

(e) **A Non-ideal Solution:** The solution that shows deviations from Raoult's law due to differences in molecular structures (i.e., size, shape, and intermolecular forces) of the components are called non-ideal solutions.
Example: Solution of ethanol in water, solution of HCl in water.

(f) Zeotropic Solution: A solution that distill with the change in composition and do not have constant boiling point is called zeotropic solution. Its components can be separated by fractional distillation. It is ideal solution that obeys Raoults law.

(g) **Heat of Hydration:** The amount of heat evolved or absorbed when one mole of gaseous ions or solute particles dissolve in water to form an infinite dilute solution.
For Ex; When 1 mole of gaseous hydrogen ions are dissolve in water forming an infinitely dilute solution, a large amount of heat is evolved.

$$H^{+}_{(g)} + \text{Water} \longrightarrow H^{+}_{(aq)} \qquad \Delta H = -1075 \text{ kJ/mol}$$

Heat of hydration depends upon the charge to size ration. In IA, heat of hydration decreases. In this group size of ions increases but charge remains the same.
In the VII A, heat of hydration decreases due to decrease in the ratio of charge to size.

(h) **Water of Crystallization:** The water molecules which combine with the compounds as they are crystallized from aqueous solution are called water molecules of crystallization or simply water of crystallization or water of hydration.
Example: $Na_2CO_3 . 10H_2O$.

(i) **Azeotropic Solution:** A solution that distills without change in composition and have constant boiling point is called azeotropic solution. Its components cannot be separated by fractional distillation. It is non-ideal solution that shows either positive or negative deviation from Raoult's law.
Example: Solution of HCl in water or solution of ethanol in water.

(j) **Conjugate Solution:** Two partially miscible liquids remain as separate layers but small quantities of these layers dissolve into each other forming solution of one another called conjugate solutions or two layers of partially miscible liquids which are solution of each other are called conjugate solutions.

Q.5 (a) What are the concentration units of solutions. Compare molar and molal solutions.
(b) One has one molal solution of NaCl and one molal solution of glucose:
(i) Which solution has greater number of particles of solute?
(ii) Which solution has greater amount of solvent?
(iii) How do we convert these concentration into weight by weight percentage?

Ans.

(a) **Concentration Units of Solution:** The units used to measure the concentration of solutions are called concentration units of solutions which are listed below:
(i) Percentage composition (%) (ii) Molarity (M)
(iii) Molality (m) (iv) Mole-fraction (X)
(v) Parts per million (ppm)

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Comparison of Molar and Molal Solution:

Molar Solution		Molar Solution	
(i)	The solution having no. of moles of solute per dm^3 of the solution.	(i)	The solution having no. of moles of solute per kg of the solvent.
(ii)	Molar solution of a substance (say sugar) is concentrated.	(ii)	Molal solution of a substance (say sugar) is dilute.
(iii)	The concentration of molar solution vary with the temperature because volume of solution is considered which depends upon temperature.	(iii)	The concentration of molal solution do not vary with the temperature because masses of solute and solvent are considered which do not depend upon temperature.
(iv)	The concentration of molar solution is calculated by formula.	(iv)	The concentration of molal solution is calculated by formula.
Molarity (M) $= \frac{\text{No. of moles of solute}}{\text{Volume of solution in dm}^3}$		Molality (m) $= \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$	

(b) (i) 1 molal NaCl solution has greater number of particles than 1 molal glucose solution.

1 molal solution means that the solutions contain one mole of solute per kg of the solvent. 1 mole of NaCl has Avogadro's no. of formula units and twice the Avogadro's no. of particles (ions) and 1 mole of glucose has Avogadro's no. of molecules. Avogadro's no. of formula unit of NaCl (being electrolyte) produces twice the Avogadro's no. of ions (particles) in solution. Avogadro's no. of molecules of glucose (1 mole) being non-electrolyte do not dissociate or ionize in solution and as a result its no. of molecules (particles) remains the same i.e., Avogadro's no.

Hence, 1 molal NaCl solution has greater number of particles than 1 molal glucose solution.

(ii) Both the solutions are molal and for molal solution we consider 1 kg of the solvent. So, both the solutions have equal amount of solvent.

(iii) For weight by weight percentage, we need mass of solute and total mass of solution and formula used is:

$$\text{Percentage of solution} = \frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$$

(a) w/w % of 1 molal NaCl solution:

Mass of NaCl (solute) = 58.5 g (1 mole)

Mass of water (solvent) = 1000 g (1 kg)

Total mass of solution = 1000 + 58.5 = 1058.5 g

$$\text{Percentage of NaCl solution} = \frac{\text{Mass of NaCl}}{\text{Total mass of solution}} \times 100$$

$$= \frac{58.5\text{ g}}{1058.5\text{ g}} \times 100 = 5.52\%$$

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(b) w/w % of 1 molal solution of glucose:

Mass of glucose (solute) = 180 g (1 mole)

Mass of water (solvent) = 1000 g (1 kg)

Total mass of solution = 1000 + 180 = 1180 g

$$\text{Percentage of glucose solution} = \frac{\text{Mass of glucose}}{\text{Total mass of solution}} \times 100$$

$$= \frac{180}{1180} \times 100 = 15.2\%$$

Q.6 Explain the following with reason?

(i) The concentration in terms of molality is independent of temperature but molarity depends upon temperature.

(ii) The sum of mole fractions of all the components is always equal to unity for any solution.

(iii) 100 g of 98% H_2SO_4 has volume of 54.34 cm^3 of H_2SO_4 because its density is 1.84 gcm^{-3}.

(iv) Relative lowering of vapour pressure is independent of the temperature.

(v) Colligative properties are obeyed when the solute is non-electrolyte and also when the solutions are dilute.

(vi) The total volume of the solution by mixing 100 cm^3 of water with 100 cm^3 of alcohol may not be equal to 200 cm^3 Justify it.

(vii) One molal solution of urea, in water is dilute as compared to one molar solution of urea. But the number of particles of the solute is same. Justify it.

(viii) Non-ideal solution don't obey the Raoult's law.

Ans.

(i) In case of molarity, we consider masses of solute and solvent. Mass is a temperature independent quantity. Hence, molality is also a temperature independent quantity.

Whereas, for molarity volume of the solution is taken and volume is a temperature dependent quantity. Hence molarity also depends upon temperature.

Note: Molar solution of a substance is concentrated at higher temperature than at lower temperature.

(ii) We have solution with two components i.e., A = solvent and B = solute. For example:

No. of moles of solvent (A) = n_A = 98 moles

No. of moles of solute (B) = n_B = 2 moles

Total no. of moles of solution = $n_A + n_B$ = n_t = 100 mole

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Mole fraction of a component = No. of moles of that components÷Total no. of moles

Mole fraction of solvent (A) $= X_A$

$$= \frac{n_A}{n_A + n_B}$$

$$= \frac{98}{100} = 0.98$$

Mole fraction of solute (B) $= X_B$

$$= \frac{n_A}{n_A + n_B}$$

$$= \frac{2}{100} = 0.02$$

Sum of mole fraction 'A' and 'B' $= X_A + X_B$

$= 0.98 + 0.02$

$= X_A + X_B$

$= 1.00$

Note: (i) The mole fraction of one component in a mixture is always less than unity.

(ii) The sum of mole fractions of all the components is always equal to unity.

(iii) The mole fraction multiplied by 100 gives mole percent.

(iv) The mole percent of one component in a mixture is always than 100.

(v) The sum of mole percents of all the components in a mixture is always equal to 100.

(iii) Mass of H_2SO_4 solution = 100 g

Density of H_2SO_4 solution = 1.84 g cm^{-3}

Volume of H_2SO_4 solution = ?

We know that:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

or $$\text{Volume} = \frac{\text{Mass}}{\text{Density}}$$

$$\text{Volume} = \frac{100}{1.84}$$

$$\boxed{\text{Volume} = 54.34 \text{ cm}^3}$$

(iv) The relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{\Delta P}{P^\circ} = X_2$$

Mole fraction of the solute is a temperature independent quantity. Mole fraction of a solute is ratio of no. of moles of solute to the total no. of moles of solute and solvent. And no. of moles does not depend upon temperature. Hence, relative lowering of vapour pressure does not depend upon temperature.

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(v) **Colligative properties when solute is non-electrolyte:** Colligative properties depends upon number of solute particles in solution. Non-electrolyte solute do not ionize in solution and its number of particles remain the same. e.g., 1 mole of urea-produces 6.02×10^{23} particles in solution.

When solute is electrolyte, it ionizes in the solution and its no. of particles increases. As a result of that Raoult's law and colligative properties are not obeyed e.g., 1 mole of NaCl produces $2(6.02 \times 10^{23})$ particles (6.02×10^{23} Na^+ ions and 6.02×10^{23} Cl^- ions) in the solution.

Colligative properties when solution is dilute: When solution is dilute, less number of solute particles far away from each other and they behave independently. And colligative properties are obeyed.

For a concentrated solution, there are greater number of solute particles which are closer to each other. Due to which attraction dominate and particles may associate. As a result of which lowering of vapour pressure is less than the ideal value.

Hence colligative properties are not obeyed for concentrated solution.

(vi) When 100 cm^3 of water and 100 cm^3 of alcohol are mixed together, the volume of the solution is slightly more than 200 cm^3. This is because forces of attraction between water-alcohol in mixture are weaker than that between water and alcohol in their pure state. Also, that is the reason why this solution shows deviation from Raoult's law.

This solution is not ideal and shows positive deviation from Raoult's law.

(vii) In one molal solution of urea, 60 g of urea is dissolved in 1000 g of water. 1000 g of water is approximately equal to its 1000 cm^3. In 1 molal solution, volume of solvent (H_2O) will be 1000 cm^3 whereas, 1 molar solution contains 60 g urea dissolved per 1000 cm^3 of solution. Means in the later solution the volume of water is less than 1000 cm^3, because solute is also included in 1000 cm^3 of solution.

Hence, number of solute particles are same in both the solutions but molal solution of urea containing greater amount of solvent (water) is dilute as compared to its molar solution.

(viii) During the formation of non-ideal solution, there is either decrease or increase of attraction between solute and solvent particles. As a result, of which the values of vapour pressure of the individual components are not proportional to their mole fraction. This is against the Raoult's law. Therefore, we say that non-ideal solutions do not obey Raoult's law.

Q.7 What are non-ideal solution? Discuss their types and give three examples of each.

Ans. Descriptive question, consult text book.

Q.8 (a) Explain fractional distillation. Justify the two curves when composition is plotted against boiling point of solutions.

(b) The solutions showing positive and negative deviations cannot be fractionally distilled at their specific compositions. Explain it.

Ans.

(a) Descriptive question, consult text book.

(b) Descriptive question, consult text book.

Q.9 (a) What are azeotropic mixtures? Explain them with the help of graphs.

(b) Explain the effect of temperature on phenol- water system.

Ans.

(a) Descriptive question, consult text book.

(b) Descriptive question, consult text book.

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Q.10 (a) What are the colligative properties? Why are they called so?

(b) What is the physical significant of K_b and K_f values of solvents?

Ans.

(a) Descriptive question, consult text book.

(b) **Molal Boiling Point Constant (K_b):** If we have one molal solution of different non-volatile and non-electrolyte solutes in H_2O, then the boiling point elevation for all the solutions will be same i.e., 0.52°C. This is called molal boiling point constant. Its value is different for different solvents but is independent of nature of solute. It units are $C° \text{ kg mol}^{-1}$.

Molal Freezing Point Constant (K_f): Freezing point depression for 1 molal solution of non-volatile and non-electrolyte solute in H_2O is same i.e., 1.86°C and is called molal freezing point constant. Its value depends upon the nature of solvent and is independent of nature of solute. Its units are $C° \text{ kg mol}^{-1}$.

(b) Descriptive question, consult text book.

Q.11 How do you explain that the lowering of vapour pressure is a colligative property? How do we measure the molar mass of a non-volatile, non-electrolyte solute in a volatile solvent?

Ans. Descriptive question, consult text book.

Q.12 How do you justify that?

(a) Boiling points of the solvents increase due to the presence of solutes.

(b) Freezing points are depressed due to the presence of solutes.

(c) The boiling point of one molal urea solution is 100.52°C but the boiling point of two molal urea solution is less than 101.04°C.

(d) Beckmann's thermometer is used to note the depression in freezing point.

(e) In summer the antifreeze solutions protect the liquid of the radiator from boiling over.

(f) NaCl and KNO_3 are used to lower the melting point of ice.

Ans.

(a) When solute is added to solvent, some of the solute molecules come to lie on the surface of solvent as well. They do not allow the solvent molecules to escape from the surface as quickly as in pure state. As a result of that vapour pressure decreases and boiling point increases.

Increase in boiling point depends upon the concentration of solute. Greater the amount of solute, greater will be the increase of boiling temperature.

(b) When solute is added into a solvent solute particles come to the lie in between solvent molecules and solution. As a result of that, distance between solvent molecules increases and forces of attraction between solvent molecules decreases. Hence solvent in solution freeze at lower temperature than pure solvent and freezing point decreases.

Therefore, we can easily say that the freezing point is depressed due to presence of solute.

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(c) Two molal urea solution is concentrated than one molal urea solution. No. of molecules in two molal urea solution is twice the Avogadro's no. Due to high concentration, molecules are closer together and there are dominant forces of attraction between them and molecules may associate. Due to which number of molecules which are free to move are less than twice the Avogadro's no. Hence, elevation in boiling is not doubled (101.4°C).

(d) Beckmann's thermometer can measure upto $\frac{1}{100}$ th of a degree i.e., 0.01 K. Since depression in freezing point for a dilute solution is small. Hence, Beckmann's thermometer can read very small changes of temperature during depression in freezing point.

(e) Ethylene glycol is an anti-freeze solutions in the water of car radiator. Due to the addition of ethylene glycol in water, its freezing point decreases and boiling point increases. In winter, it prevents water from freezing and in summer, it prevents water from boiling over.

(f) NaCl and KNO_3 being electrolytes and highly soluble in water. They dissolve and produces double the number of ions than formula units. Due to which freezing point is depressed to greater extent. This mixture is also used to melt the ice from roads in winter.

Q.13 What is Raoult's law? Give its three statements. How this law can help us to understand the idealility of a solution.

Ans. Descriptive question, consult text book.

Q.14 Give graphical explanation for elevation of boiling point of a solution. Describe one method to determine the boiling point elevation of a solution.

Ans. Descriptive question, consult text book.

Q.15 Freezing points of solutions are depressed when non-volatile solutes present in volatile solvents. Justify it. Plot a graph to elaborate your answer. Also give one method to record the depression of freezing point of a solution.

Ans. Detailed question. For answer, consult text book.

Q.16 Discuss the energetics of solution. Justify the heats of solutions as exothermic or endothermic properties.

Ans. Descriptive question, consult text book.

Q.17 (a) Calculate the molarity of glucose solution when 9g of it is dissolved in 250 cm^3 of solution.

(b) Calculate the mass of urea in 100 g of water in 0.3 molal solution.

(c) Calculate the concentration of solution in molality kg^{-1} which is obtained by mixing 250 g of 20% solution of NaC1 with 200 g of 40% solution of NaCl.

Ans.

(a) The volume of solution has to be taken in dm^3.

Mass of glucose dissolved (W_2) = 9.0 g
Volume of solution = 250 cm^3
= 0.25 dm^3
Molar mass of glucose = 180.0 g mol
Molarity of solution = ?

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$$\text{Molarity (M)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution in dm}^3}$$

Substituting the values:

$$\text{Malarity (M)} = \frac{9.00\text{ g}}{180.0\text{ g/mol}} \times \frac{1}{0.25\text{ dm}^3}$$

$$\text{Molarity (M)} = \frac{9}{180 \times 0.25}\text{ moles dm}^{-3}$$

$$\text{Molarity (M)} = 0.2\text{ M}$$

(b) We need the mass of solvent in kg.

Mass of water as a solvent = 100.00 g

$$\text{Mass of solvent in kg} = \frac{100}{1000} = 0.1\text{ kg}$$

Molality of solution (m) = 0.3 m

Molar mass of urea = 60.0 g mol^{-1}

Mass of urea dissolved = ?

$$\text{Molality (m)} = \frac{\text{Mass of urea}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in (kg)}}$$

Putting values:

$$0.3\text{ mol kg}^{-1} = \frac{\text{Mass of urea}}{60.00\text{ g mol}^{-1}} \times \frac{1}{0.1\text{ kg}}$$

$$\text{Mass of urea} = 0.3 \times 60.00 \times 0.1$$

$$\text{Mass of urea} = 1.8\text{ g}$$

(c) 1st solution:

% of NaCl solution = 20%

Mass of 20% solution = 250 g

Concentration of solution = ?

20% of NaCl solution means that:

100 g of solution has NaCl = 20 g

$$\text{1 g of solution has NaCl} = \frac{20}{100}\text{ g}$$

$$= \frac{20}{100} \times 250\text{ g}$$

250 g of solution has NaCl = 50 g

2nd solution:

% of NaCl solution = 40

Mass of 40% NaCl solution = 200 g

100 g of solution has NaCl = 40 g

$$\text{1 g of solution has NaCl} = \frac{40}{100}\text{ g}$$

$$\text{200 g of solution has NaCl} = \frac{40}{100} \times 200$$

$$= 80\text{ g}$$

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Mass of NaCl in both solutions = 50 + 80 = 130 g
Total mass of both the solutions = 200 + 250 = 450 g
Mass of solvent = 450 – 130 = 320 g = 0.32 kg

$$\text{Molality} = \frac{\text{Mass of solute}}{\text{Molar mass}} \times \frac{1}{\text{Mass of solvent in kg}}$$

Putting the values:

$$\text{Molality} = \frac{130}{58.5} \times \frac{1}{0.32} = 0.71 \text{ m}$$

Q.18 (a) An aqueous solution of sucrose has been labeled as one molal. Find the mole fraction of the solute and the solvent.

(b) You are provided with 80 % H_2SO_4 w/w having density 1.8 g cm^{-3}. How much volume of this sulphuric acid sample is required to obtain 1 dm^3 of 20% w/w H_2SO_4 whose density is 1.25 g cm^{-3}.

Ans.

(a) Name of compound = Sucrose ($C_{12}H_{22}O_{11}$)
Molar mass of sucrose = 342 g mol^{-1}
Since, the solution is 1 molal, so 342 g is dissolved in 1000 g of H_2O.

Hence Mass of sucrose dissolved = 342 g
Mass of H_2O taken = 1000 g
Number of moles of sucrose = 1
Mole fraction of solvent = ?
Mole fraction of solute = ?

First of all calculate no. of moles of water.

$$\text{Number of moles of } H_2O = \frac{\text{Mass of water taken}}{\text{Molar mass of water}}$$

Putting values:

$$\text{No. of moles of } H_2O = \frac{1000}{18} = 55.55$$

And no. of moles of sucrose is 1.
Now we calculate mole fraction of sucrose.

$$\text{Mole fraction of sucrose } (X_{\text{sucrose}}) = \frac{\text{No. of moles of sucrose}}{\text{Total no. of moles}}$$

Putting the values:

$$\text{Mole fraction of sucrose } (X_{\text{sucrose}}) = \frac{1}{55.51 + 1} = \boxed{0.0176}$$

Similarly calculate mole fraction of H_2O.

$$\text{Mole fraction of water } (X_{H_2O}) = \frac{\text{Number of moles of } H_2O}{\text{Total no. of moles}}$$

Putting the values:

$$\text{Mole fraction of water } (X_{H_2O}) = \frac{55.55}{55.55 + 1} = \boxed{0.9823}$$

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(b) The solution of this numerical is to be done in two stages:

(i) Conversion of 80% H_2SO_4 to molarity:

% of concentrated H_2SO_4 = 80.00

Density of concentrated H_2SO_4 = 1.8 g cm^{-3}

It means:

1 cm^3 of H_2SO_4 has mass = 1.8 g

1000 cm^3 of H_2SO_4 has mass = 1.8×1000 = 1800 g

1800 g of concentrated H_2SO_4 is 80% of H_2SO_4.

100 g of concentrated solution of H_2SO_4 contains H_2SO_4 = $\frac{80}{100} \times 1800$ = 1440 g

$$\text{Number of moles of } H_2SO_4 = \frac{\text{Mass of } H_2SO_4}{\text{Molar mass of } H_2SO_4}$$

Putting the values:

$$\text{Number of moles of } H_2SO_4 = \frac{1440 \text{ g}}{98 \text{ g mol}^{-1}} = 14.7 \text{ mole}$$

It means 14.7 moles of H_2SO_4 is present in 1000 cm^3 of solution, hence, it is 14.7 molar H_2SO_4.

Conversion of 20% H_2SO_4 in molarity:

% of dilute H_2SO_4 = 20

Density of dilute H_2SO_4 = 1.25 g cm^{-3}

It means:

1 cm^3 of H_2SO_4 has mass = 1.25 g

1000 g cm^3 of H_2SO_4 has mass = 1.25×1000 = 1250 g

1250 g of dilute H_2SO_4 is 20% H_2SO_4.

100 g of dilute solution contains H_2SO_4 = 20 g

1 g of dilute solution of H_2SO_4 has H_2SO_4 = $\frac{20}{100}$ g

1250 g of dilute solution of H_2SO_4 has H_2SO_4 = $\frac{20}{100} \times 1250$ = 250 g

$$\text{No. of moles of } H_2SO_4 = \frac{\text{Mass of } H_2SO_4}{\text{Molar mass}}$$

Putting the values:

$$\text{No. of moles of } H_2SO_4 = \frac{250 \text{ g}}{98 \text{ g mol}^{-1}} = 2.55 \text{ mol}$$

Now, we have to dilute 14.7 M solution to 2.55 M H_2SO_4. For this purpose, use the dilution formula.

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(ii) Conc. H_2SO_4 = Dil. H_2SO_4

$M_1V_1 = M_2V_2$

Putting the values:

$$14.7 \times V_1 = 2.55 \times 1000$$

$$V_1 = \frac{2.55 \times 1000}{14.7}$$

$$V_1 = 173.5 \text{ cm}^3$$

So, 173.5 cm^3 of conc. H_2SO_4 is diluted up to 1000 cm^3 to get the solution of required molarity. In this way 14.7 M H_2SO_4 is converted to 2.55 M H_2SO_4.

Q.19 250 cm^3 of 0.2 molar K_2SO_4 solution is mixed with 250 cm^3 of 0.2 molar KCl solution. Calculate the molar concentration of K^+ ions in the solution.

Ans. 250 cm^3 of 0.2 molar K_2SO_4 solution has 0.4 moles $K^{\oplus}$ ion. Because each formula unit of K_2SO_4 has two $K^{\oplus}$ ions.

250 cm^3 of 0.2 molar KCl solution has 0.2 moles $K^{\oplus}$ ion.

Because one formula unit of KCl has one $K^{\oplus}$ ion.

When two solutions are mixed then 0.6 moles $K^{\oplus}$ ions may be present if the volume remains 250 cm^3. Since after mixing 500 cm^3 volume is obtained, so the conc. of $K^{\oplus}$ ions become half of 0.6 molar i.e., 0.3 molar.

Q.20 5 g of NaCl is dissolved in 1000 g of water, the density of resulting solution is 0.997 gcm^{-3} Calculate the Molarity and mole fractions of this solution. Assume that the volume of the solution is equal to that of solvent.

Ans.

(i) Calculation of molality (m):

Mass of NaCl = 5 g

Mass of H_2O = 1000 g = 1 kg

$$\text{Molality of NaCl (m)} = \frac{\text{Mass of NaCl}}{\text{Molar mass of NaCl}} \times \frac{1}{\text{Mass of solvent in (kg)}}$$

$$\text{Molality of NaCl (m)} = \frac{5}{58.5} \times \frac{1}{1 \text{ kg}} = 0.0854 \text{ molal}$$

(ii) Calculations of molarity (M):

Density of solution = 0.997 g cm^{-3}

Total mass of solution = 1005 g

$$d = \frac{m}{V}$$

$$V = \frac{m}{d}$$

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Putting the values:

$$V = \frac{1005}{0.997} = 1008.02 \text{ cm}^3$$

Volume of solution in dm^3 = 1.00802 dm^3

$$\text{Molarity (M)} = \frac{\text{Mass of NaCl}}{\text{Molar mass}} \times \frac{1}{1.00802}$$

Molar mass of NaCl = 58.5 mol^{-1}

Putting the values:

$$\text{Molarity (M)} = \frac{5}{58.5} \times \frac{1}{1.00802} = \boxed{0.084}$$

(iii) Calculation of Mole Fraction:

$$\text{No. of moles of NaCl} = \frac{5}{58.5} = 0.0854$$

$$\text{No. of moles of } H_2O = \frac{1000}{18} = 55.55$$

$$X_{NaCl} = \frac{\text{No. of moles of NaCl}}{\text{No. of moles of NaCl} + \text{No. of moles of } H_2O}$$

Putting the values:

$$X_{NaCl} = \frac{0.0854}{0.0854 + 55.5}$$

$$= \frac{0.0854}{55.5854} = \boxed{0.000153}$$

$$X_{H_2O} = \frac{55.55}{55.5854} = \boxed{0.999}$$

Q.21 4.675 g of a compound with empirical formula C_3H_3O, was dissolved in 212.5 g of pure benzene. The freezing point of the solution was found 1.02°C less than that of pure benzene. The molal freezing point constant of benzene is 5.1°C. Calculate:

(i) the relative molar mass

(ii) the molecular formula of the compound

Ans. Mass of solute dissolved (W_2) = 4.675 g

Mass of solvent benzene (W_1) = 212.5 g

Depression of F.P. of solution (ΔT_f) = 1.02°C

Molar F.P constant of solvent (K_f) = 5.1°C

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(i) Relative molar mass of solute (M_2):

$$M_2 = \frac{K_f}{\Delta T_f} \cdot \frac{1000\ W_2}{W_1}$$

$$= \frac{5.1°C \times 1000 \times 4.675\ g}{1.02\ C° \times 212.5\ g}$$

$$= \frac{5.1 \times 1000 \times 4.675}{1.02 \times 212.5}$$

$$M_2 = \frac{23842.5}{216.75} = 110\ g\ mol^{-1}$$

(ii) Empirical formula $= C_3H_3O$

Empirical formula mass $= 36 + 3 + 16 = 55$

Molar mass $= n$(E.F. mass)

$110 = n(55)$

$n = \frac{110}{55} = 2$

Molecular formula of the compound $= 2$(E.F.)

$= 2(C_3H_3O)$

Hence, the molecular formula of the compound= $\boxed{C_6H_6O_2}$

Q.22 The boiling point of a solution containing 0.2 g of a substance 'A' in 20 g of ether (molar mass = 74) is 0.17 K higher than that of pure ether. Calculate the molar mass of 'A'. Molal boiling point constant of ether is 2.16 K.

Ans. Mass of the solute A (W_2) = 0.2 g

Mass of the solvent ether (W_1) = 20.0 g

Elevation of B.P. of solution (ΔT_b) = 0.17 k

Molal B.P. constant of ether (K_b) = 2.16 k

Molar mass of A (M_2) = ?

$$M_2 = \frac{K_b}{\Delta T_b} \cdot \frac{1000\ W_2}{W_1}$$

$$= \frac{2.16\ K \times 1000 \times 0.2\ g}{0.17\ K \times 20\ g}$$

$$M_2 = \frac{132}{3.4} = \boxed{127.0\ g\ mol^{-1}}$$

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Q.23 3 g of a non-volatile, non-electrolyte solute 'X' is dissolved in 50 g of ether (molar mass 74) at 293 K. The vapour pressure of ether falls from 442 torr to 426 torr under these conditions. Calculate the molecular mass of the solute X.

Ans. Mass of solute 'X' dissolved (W_2) = 3.00 g

Mass of solvent ether (W_1) = 50.00 g

Molar mass of ether (M_1) = 74.00 g mol^{-1}

Vapour pressure of pure ether (P°) = 442 torr

Vapour pressure of solution (P°) = 426 torr

Lowering of vapour pressure (ΔP) = 442 – 426 = 16 torr

Molar mass of 'X' (M_2) = ?

$$\frac{\Delta P}{P^\circ} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

$$M_2 = \frac{W_2 \times M_1 \times P^\circ}{\Delta P \times W_1}$$

$$= \frac{3.0\ g \times 74\ g\ mol^{-1} \times 442\ torr}{16\ torr \times 50.0\ g}$$

$$= \frac{3 \times 74 \times 442}{16 \times 50}\ g\ mol^{-1}$$

$$= \frac{98124}{800}\ g\ mol^{-1}$$

$$M_2 = \boxed{122.6\ g\ mol^{-1}}$$

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1. Any mixture having uniform composition and single phase is called solution.

2. The solution which contains two components is called Binary solution.

3. The substance which is present in large quantity in solution is called solvent and the substance present in small quantity is called solute.

4. The number of moles of solute dissolved per dm^3 of solution is called molarity.

5. The number of moles of solute dissolved per kg of solvent is called molality.

6. One molar solution of sugar is sweeter than one molal solution.

7. The sum of the mole fraction of all components of a solution must be equal to one (unity).

8. The number of parts by mass or volume of solute per million parts by mass or volume of solution is called ppm.

9. Phenol and water are partially miscible whereas alcohol and water are completely miscible.

10. Benzene and water are immiscible.

11. Raoults law is obeyed in case of dilute solutions.

12. The temperature at which two conjugate solutions merge into one another is called critical solution temperature or consulate temperature.

13. The liquid mixture which distills with a change in composition is called zeotropic mixture.

14. The liquid mixture which boils at constant temperature and distills over without change in composition at any pressure like a chemical compound is called azeotropic mixture.

15. The elevation of the boiling point when 1 mole of solute is dissolved in one kg of solvent is called molal boiling point constant or Ebullioscopic constant.

16. Equimolal solution of different non-electrolytes increase the boiling point equally.

17. The amount of heat evolved when one mole of vapours are condensed to a liquid at constant temperature is called latent heat of condensation.

18. The depression in the freezing point when 1 mole of solute is dissolved in one kg of solvent is called molal freezing point constant or cryoscopic constant.

19. Units of $K_b = C^\circ \text{ kg mol}^{-1}$.

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20. Units of $K_f = C° \text{ kg mol}^{-1}$.

21. The process in which solvent molecules surround and interact with the solute particles is called solvation.

22. The process in which water molecules surround and interact with the solute particles is called hydration.

23. Copper sulphate is penta hydrated.

24. Washing soda is deca hydrated.

25. Epsom salt is hepta hydrated.

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CHAPTER 9

SOLUTIONS

MULTIPLE CHOICE QUESTIONS

1. 18 g glucose is dissolved in 90 g of water. The relative lowering of vapour pressure is equal to:

(a) $\frac{1}{5}$ **(b)** 5.1

(c) $\frac{1}{51}$ **(d)** 6

2. A solution of glucose is 10%. The volume to which 1g mole of it dissolved will be:

(a) 1 dm^3 **(b)** 1.8 dm^3

(c) 200 cm^3 **(d)** 900 cm^3

3. Which of the following liquid pairs will obey the Raoult's law:

(a) $C_2H_5OH + H_2O$ **(b)** $CH_3COCH_3 + CHCl_3$

(c) $C_2H_5I + C_2H_5Br$ **(d)** $HCl + H_2O$

4. 10g of NaOH has been dissolved per dm^3 of solution. The molarity of solution is:

(a) 0.5 M **(b)** 0.25 M

(c) 1 M **(d)** 2 M

5. The sum of mole fraction of all the components of solution is always equal to:

(a) Unity **(b)** 100

(c) Less than one **(d)** Less than 100

6. Which of the following concentration unit is used for very dilute solutions:

(a) Molarity **(b)** Normality

(c) Molality **(d)** ppm

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7. Which of the following is affected by temperature change:

(a) Molality **(b)** Molarity

(c) Mole fraction **(d)** None of these

8. The substance which has water of crystallization in it, is called:

(a) Hydrate **(b)** Hydride

(c) Hydrolysis **(d)** Complex

9. Hydrolysis of CH_3COOK will produce:

(a) Acidic solution **(b)** Basic solution

(c) Neutral solution **(d)** None of these

10. The molarity of 2% $\frac{W}{V}$ NaOH solution is:

(a) 2 **(b)** 0.25

(c) 0.05 **(d)** 0.5

11. If 9.8g H_2SO_4 is present in one dm^3 of solution, the solution is:

(a) 0.1 N **(b)** 0.1 M

(c) 0.1 m **(d)** 0.5 M

12. Which one of the following salts do not hydrolyse:

(a) $CuSO_4$ **(b)** Na_2CO_3

(c) Na_2SO_4 **(d)** $Al_2(CO_3)_3$

13. An aqueous solution boil at 100.52°C. It should freeze at:

(a) 0°C **(b)** −1.86°C

(c) −2°C **(d)** +1.86°C

14. 15g urea is dissolved in 180 cm^3 of water. The relative lowering of vapour pressure will be:

(a) 0.024 **(b)** 25.024

(c) 2.5 **(d)** 10.25

15. Which has maximum freezing point:

(a) 1m NaCl **(b)** 1m KCl

(c) 1m $CaCl_2$ **(d)** 1m Urea

16. Which cation has least heat of hydration:

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(a) Li^+ **(b)** Na^+

(c) K^+ **(d)** Mg^{+2}

17. 10% aqueous solution of glucose freezes at:

(a) 0°C **(b)** Less than 0°C

(c) Greater than 0°C **(d)** Greater than 10°C

18. A mixture of benzene and toluene form:

(a) Ideal solution **(b)** Non-ideal solution

(c) Azeotropic mixture **(d)** Suspension

19. Which pair of mixture is called ideal solution:

(a) $C_6H_5Cl + C_6H_5Br$ **(b)** $H_2O + C_2H_5OC_2H_5$

(c) $C_2H_5OH + H_2O$ **(d)** $HCl + H_2O$

20. In a solution 7.8g benzene and 46g toluene ($C_6H_5CH_3$) is present, the mole fraction of benzene is:

(a) $\frac{1}{2}$ **(b)** $\frac{1}{3}$

(c) $\frac{1}{5}$ **(d)** $\frac{1}{6}$

answers

1.	(c)	**2.**	(b)	**3.**	(c)	**4.**	(b)	**5.**	(a)
6.	(d)	**7.**	(b)	**8.**	(a)	**9.**	(b)	**10.**	(d)
11.	(b)	**12.**	(c)	**13.**	(b)	**14.**	(a)	**15.**	(d)
16.	(c)	**17.**	(b)	**18.**	(a)	**19.**	(a)	**20.**	(d)

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