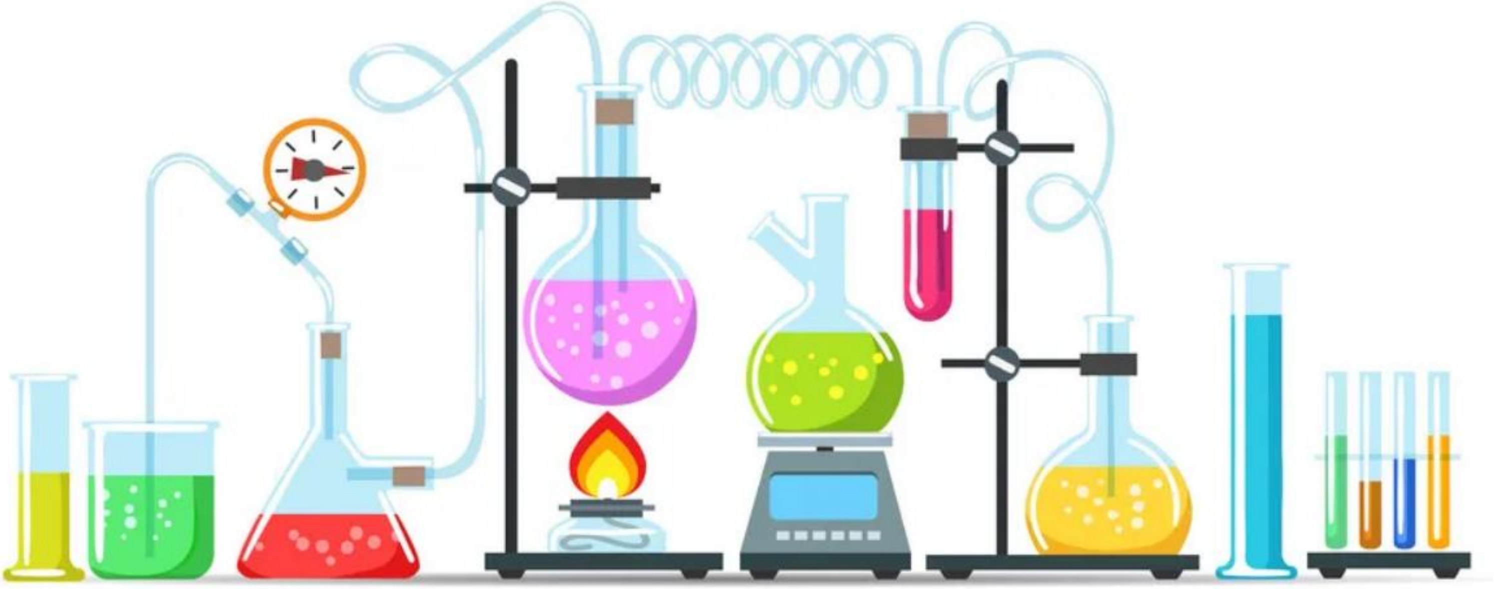
# CHEMISTRY

## CHAPTER 2: SOLUTIONS



# SOLUTIONS

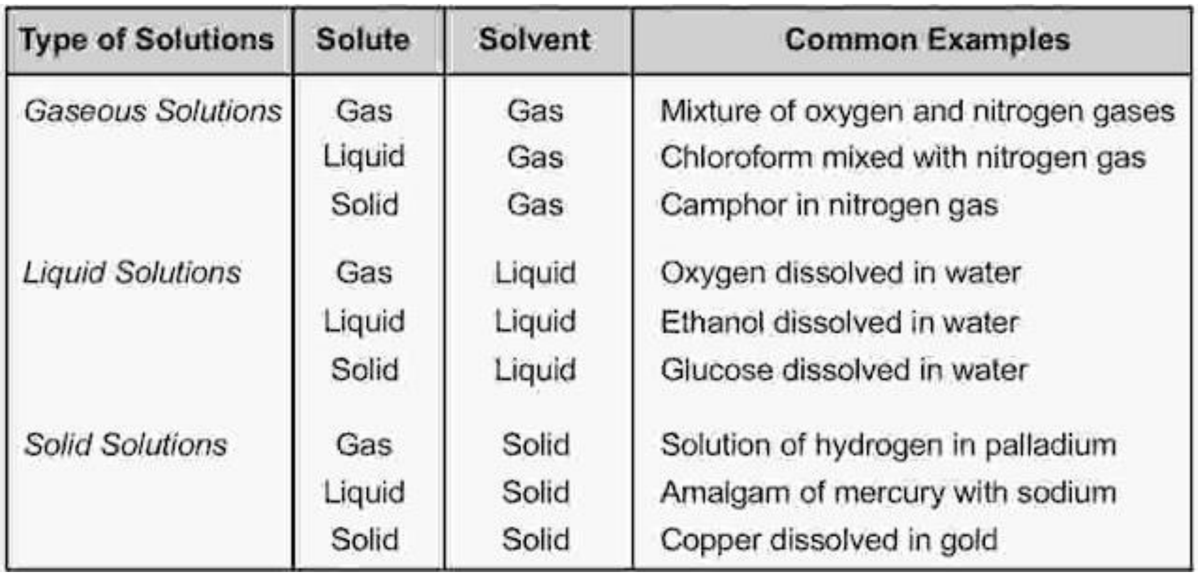
## Introduction:

In this chapter, we will discuss about liquid solutions and their formation. This will be followed by studying the properties of solutions, like vapour pressure and colligative properties. We will begin with types of solutions and expressions for concentration of solutions in different units.

Thereafter, we will state and explain Henry's law and Raoult's law, distinguish between ideal and non-ideal solution and deviation of real solutions from Raoult's law. We will also discuss abnormal colligative properties alongwith association and dissociation of solute.

## Types of Solutions

All the three states of matter (solid, liquid and gas) may behave either as solvent or solute. When a solution is composed of only two chemical substances, it is termed as binary solution. Depending upon the state of solute or solvent, binary solutions can be classified as



| Type of Solutions | Solute | Solvent | Common Examples |
|---|---|---|---|
| *Gaseous Solutions* | Gas | Gas | Mixture of oxygen and nitrogen gases |
| | Liquid | Gas | Chloroform mixed with nitrogen gas |
| | Solid | Gas | Camphor in nitrogen gas |
| *Liquid Solutions* | Gas | Liquid | Oxygen dissolved in water |
| | Liquid | Liquid | Ethanol dissolved in water |
| | Solid | Liquid | Glucose dissolved in water |
| *Solid Solutions* | Gas | Solid | Solution of hydrogen in palladium |
| | Liquid | Solid | Amalgam of mercury with sodium |
| | Solid | Solid | Copper dissolved in gold |

## Some Important Definitions

- **Mixture** - When two or more chemically non-reacting substances are mixed, they form mixture.
- **Heterogeneous Mixture** - It consists of distinct phases, and the observed properties are just the sum of the properties of individual phases.
- **Homogeneous Mixture** - It consists of a single phase which has properties that may differ from one of the individual components.

- **Solution** - The homogeneous mixture of two or more components such that at least one component is a liquid is called solution.

- **Solvent** - It is the constituent of solution which has same physical state as that of solution and generally present in greater amount than all the other components.

- **Solute** - The component of a solution other than solvent is called solute, may or may not have same physical state as that of solution. Generally it is in smaller amount.

  ***Example*** - In a sugar syrup (liquid solution) containing 60% sugar (solid) and 40% water (liquid), water is termed as solvent, due to same physical state as that of solution.

## Expressing the Strength of Solution

For a given solution the amount of solute dissolved per unit volume of solution is called concentration of solute. Strength of solution is the amount of solute in grams dissolved in one litre of solution. It is generally expressed in g/litre.

Other methods of expressing the strength of solution are:

1. **Mass percentage –**

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

$$\text{Mass \% of solvent} = \frac{\text{Mass of solvent}}{\text{Total mass of solution}} \times 100$$

2. **Volume percentage –**

$$\text{Volume \% of solute} = \frac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$$

$$\text{Volume \% of solvent} = \frac{\text{Volume of solvent}}{\text{Total volume of solution}} \times 100$$

3. **Molality (m) -** It is no. of moles of solute dissolved in 1 kg of the solvent.

$$\text{m} = \frac{\text{(Number of moles of solute)}}{\text{(Mass of solvent \{in kg\})}}$$

4. **Molarity (M) -** It is no. of moles of solute dissolved in 1 litre of solution.

$$\text{M} = \frac{\text{(Number of moles of solute)}}{\text{(Mass of soution \{in litre\})}}$$

5. **Normality (N) -** It is no. of gram-equivalents of solute dissolved in 1 litre of solution

$$\text{N} = \frac{\text{(Number of gram equivalents of solute)}}{\text{(Volume of solution \{in litre\})}}$$

6. **Formality -** Ionic solutes do not exist in the form of molecules. These molecular mass is

expressed as Gram-formula mass. Molarity for ionic compounds is actually called as **formality.**

7. **Mole fraction –**

$$\text{Mole fraction of solute } = \frac{(\text{Number of moles of solute})}{(\text{Total moles of solution})}$$

$$\text{Mole fraction of solvent } = \frac{(\text{Number of moles of solvent})}{(\text{Total moles of solution})}$$

For a binary solution,

mole fraction of solute + mole fraction of solvent = 1.

8. **Parts per million (ppm) –**

It is defined in two ways

$$\text{ppm} = \text{mass fraction} \times 10^6$$

$$\text{ppm} = \text{mole fraction} \times 10^6$$

## Solubility

**Solubility** of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature. It depends upon the nature of solute and solvent as well as temperature and pressure. Let us consider the effect of these factors in solution of a **solid** or a **gas** in a **liquid**.

### 1. Solubility of Solid in Liquid

A solute dissolves in a solvent if the intermolecular interactions are similar in them, i.e., like dissolves like. Polar solute dissolves in polar solvent and non-polar solute in non-polar solvent. For e.g., sodium chloride and sugar dissolves readily in water and napthalene and anthracene dissolves readily in benzene.

Solute + Solvent ⟶ Solution

i. **Dissolution:** When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is called **dissolution**.

ii. **Crystallization**: Some solute particles collide with solute particles in solution and get separated out. This process is called **crystallization**.

iii. **Saturated solution**: Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution.**

iv. **Unsaturated solution:** An unsaturated solution is one in which more solute can be dissolved at the same temperature.

v. **Effect of temperature**: In general, if in a nearly saturated solution, the dissolution process is endothermic, the solubility should increase with rise in temperature, if it is exothermic, the solubility should decrease with rise in temperature.

vi. **Effect of pressure**: Solids and liquids are highly incompressible, so pressure does not have any significant effect on solubility of solids and liquids.

vii. **Supersaturated solution**: When more solute can be dissolved at higher temperature in a saturated solution, then the solution becomes supersaturated.

## 2. Solubility of Gas in Liquid

All gases are soluble in water as well as in other liquids to a greater or lesser extent. The solubility of a gas in liquid depends upon the following factors Nature of the gas, Nature of solvent, Temperature and Pressure.

Generally, the gases which can be easily liquified are more soluble in common solvents. For e.g., CO2 is more soluble than hydrogen or oxygen in water. The gases which are capable of forming ions in aqueous solutions are much more soluble in water than other solvents. For e.g., HCl and NH3 are highly soluble in water but not in organic solvents (like benzene) in which they do not ionize.

i. **Effect of temperature:** Solubility of most of the gases in liquids decreases with rise in temperature. In dissolution of a gas in liquid, heat is evolved and thus this is an exothermic process. The dissolution process involves dynamic equilibrium and thus follows **Le Chatelier's** principle. As dissolution is exothermic the solubility of gas should decrease with rise in temperature.

ii. **Effect of pressure: Henry's law**: At constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas.

$$p = KH\ x,$$

KH = Henry's law constant.

### Applications of Henry's law

1. In manufacture of soft drinks and soda water, $CO_2$ is passed at high pressure to increase its solubility.
2. To minimise the painful effects accompanying the decompression of deep sea divers. $O_2$ diluted with less soluble. He gas is used as breathing gas.
3. At high altitudes, the partial pressure of $O_2$ is less then that at the ground level. This leads to low concentrations of $O_2$ in the blood of climbers which causes '**anoxia**'.

## Vapour Pressure of Solution

It is the pressure exerted by vapour on the surface layer of liquid at equilibrium between vapour and liquid.

### Factors affecting Vapour Pressure

i. **Nature of liquid -** Liquid with higher intermolecular attraction forces form less amount of vapour and hence lower vapour pressure and vice-versa.

ii. **Temperature -** Vapour pressure increases with temperature of liquid. This is because, as temperature increases, kinetic energy of the molecules increases, hence, more molecules leave the surface of the liquid and come into vapour phase.

## Raoult’s Law

According to Raoult’s law, for a solution of volatile liquids, the relative lowering of vapour pressure of solution is directly proportional to its mole fraction of dissolved solvent in solute.

$$\frac{P^\circ - P}{P^\circ} = X_A$$

## Ideal and Non-Ideal Solution

The binary liquid-liquid solution may be classified into two types :

(1) Ideal solutions

(2) Non-ideal solutions

## 1) Ideal Solutions

An **ideal solution** may be defined as the solution which obeys Raoult’s law over the entire range of concentration.

a) Such solutions are formed by mixing two components which are identical in molecular size, in structure and have almost identical intermolecular forces.

b)The intermolecular interactions between the components (A – B attractions) are of same magnitude as the intermolecular interactions in pure components (A- A and B-B attractions).

According to Raoult’s law, the partial vapour pressure of two components of the solution may be given as :

$$pA = pA^\circ xA$$

$$pB = pB^\circ xB$$

Total pressure p is given by

$$p = pA + pB$$

$$p = p_A^\circ x_A + p_B^\circ x_B$$

The ideal solutions have also the following characteristics:

**1) Heat change on mixing is zero:** Since there is no change in magnitude of the attractive forces in the two components present, the heat change on mixing i.e. $\Delta_{mixing}H$ in such solutions must be zero.

**2) Volume change on mixing is zero:** In ideal solutions, the volume of the solution is the sum of the volumes of the components before mixing i.e. there is no change in volume on mixing or $\Delta_{mixing} V$ is zero.

The solutions generally tends to become ideal when they are dilute.

The characteristics of an ideal solution may be summed up as follows

(i) It must obey Raoult's law.
(ii) $\Delta_{mixing} H$ should be zero.
(iii) $\Delta_{mixing} V$ should be zero.

### Example of Ideal Solutions

(i) Benzene and toluene
(ii) n-hexane and n-heptane
(iii) Bromoethane and iodoethane
(iv) Chlorobenzene and bromobenene

Solutions which obey Raoult's law are called **ideal liquid solution.**

### Composition in Vapour Phase

The composition of vapour phase in equilibrium with the solution is determined by the partial pressure of the components. If $y_1$and $y_2$ are the mole fraction of the two components 1 and 2 respectively in the vapour phase, then according to Dalton's law of partial pressures:

Partial pressure of a component =Mole fraction of the component x Total pressure

$$p_1 = y_1\, p$$

$$p_2 = y_2\,p$$

In general, $P_i = y_i\,p_{total}$

Mole fraction of component 1 in vapour phase $y_1 = p_1/p$

Mole fraction of component 2 in vapour phase, $y_2 = p_2/p$

Mole fraction of a component in vapour phase =

Partial vapour pressure of component / Total Vapour Pressure

## 2) Non-Ideal Solutions

The solutions which do not obey Raoult's law over the entire range of concentration are called **non-ideal solutions**. Therefore, for such solutions

$$p_A \neq p_A^\circ x_A$$

$$p_B \neq p_B^\circ x_B$$

The vapour pressure of such solutions is either higher or lower than that predicted by Raoult's law.

In non-ideal solutions, there is a noticeable change in volume and heat energy when the two components are mixed.

Most of the solutions are non-ideal because they deviate from ideal behaviour to more or less extent.

Thus, for non-ideal solutions,

a) none of the components obey Raoult's law over the entire composition range, i.e.

$p_A \neq p_A^\circ x_A$ and $p_B \neq p_B^\circ x_B$

b) (i) $\Delta_{mixing} H$ is not equal to zero

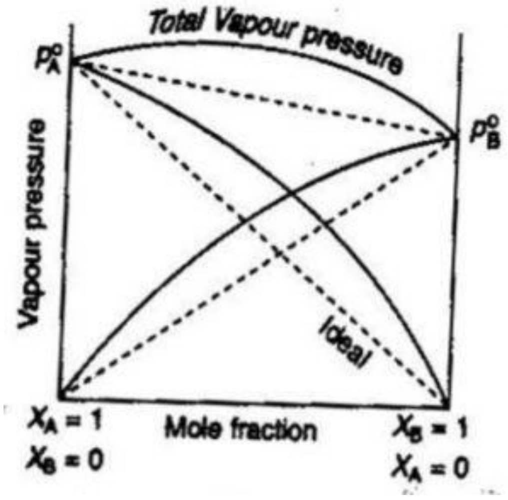
(ii) $\Delta_{mixing} V$ is not equal to zero

| Ideal solution | Non-Ideal solution |
|---|---|
| The interactions between the components are similar to those in the pure components. | The interaction between the components are different from those of the pure components. |
| There is no enthalpy change on mixing.<br>$\Delta$mixingH =0 | There is no enthalpy change on mixing.<br>$\Delta$mixingH $\neq$ 0 |
| There is no volume change on mixing.<br>$\Delta$mixing V =0 | There is no volume change on mixing.<br>$\Delta$mixing V $\neq$ 0 |
| Each component obeys Raoult's law at all temperatures and concentrations,<br>$pA = pA^{\circ}xA$ and $pB = pB^{\circ}xB$ | Their components do not obey Raoult's law. They show positive and negative deviations from Raoult's law.<br>$pA \neq pA^{\circ}\, xA$ and $pB \neq pB^{\circ}\, xB$ |

## Types of Non-ideal Solutions

Non-ideal solutions show positive and negative deviations from the ideal behaviour depending upon their nature.

### (1) Non-Ideal solutions showing positive deviations from Raoult's law



Consider a binary solution of two components A and B.

If the A-B interactions in the solutions are weaker than the A-A and B-B interactions in the two liquids forming the solution, then the escaping tendency of A and B types of molecules from the solution becomes more than from pure liquids. As a result, each component of solution has a partial vapour pressure greater than expected on the basis of Raoult's law. The total vapour pressure will be greater than corresponding vapour pressure expected in case of ideal solution of the same composition. This type of behaviour of solution is described as positive deviations from Raoult's law.

$$p_A > p_A^\circ x_A \text{ and}$$

$$p_B > p_B^\circ x_B$$

The total vapour pressure,

$$p = p_A + p_B \text{ is always greater than } (p_A^\circ x_A + p_B^\circ x_B)$$

Examples of solutions showing positive deviations are :

(i) Ethyl alcohol and cyclohexane
(ii) Acetone and carbon disulphide
(iii) Benzene and acetone
(iv) Carbon tetrachloride and choloroform
(v) Acetone and ethyl alcohol
(vi) Ethyl alcohol and water.

## Explanation for positive deviations

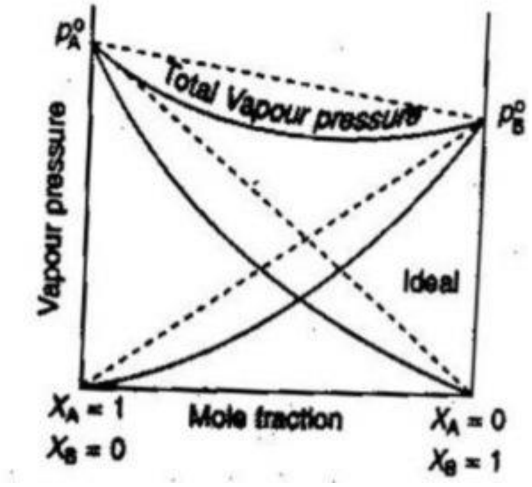
In ethyl alcohol, the molecules are held together due to hydrogen bonding. When cyclohexane is added to ethyl alcohol, the molecules of cyclohexane tend to occupy the spaces between ethyl alcohol molecules. Consequently, some hydrogen bonds in alcohol molecules break and the attractive forces in alcohol molecules are weakened. The escaping tendency of alcohol and cyclohexane molecules from the solution increases. Consequently, the vapour pressure of the solution is greater than the vapour pressure as expected according to Raoult's law.

(i) $\Delta_{mixing} H$ is positive because energy is required to break A-A or B-B attractive forces. Therefore, dissolution process is endothermic.

(ii) Because of the decrease in the magnitude of intermolecular forces in solutions, the molecules will be loosely held and, therefore, there will be increase in volume on mixing. Thus, $\Delta_{mixing} V$ will be positive.

(iii) Since the dissolution process in endothermic, heating will increase the solubility of such a solution.

## (2) Non-Ideal solutions showing negative deviations from Raoult's law.



In such solutions, the A-B interactions are stronger than the A-A and B-B interactions present in the two liquids forming the solution. Due to stronger A-B interactions, the escaping tendency of A and B types of molecules from the solution becomes less than from pure liquids. Consequently, each component of the solution has a partial vapour pressure less than expected on the basis of Raoult's law. As a result , the total vapour pressure becomes less than the corresponding vapour pressure expected in case of ideal solution.

$$p_A < p_A^\circ x_A \text{ and}$$

$$p_B < p_B^\circ x_B$$

$$p = p_A + p_B \text{ is always less than } (p_A^\circ x_A + p_B^\circ x_B)$$

**Examples of Negative Deviation**

(i) Acetone and chloroform
(ii) Chloroform and diethyl ether
(iii) Chloroform and nitric acid
(iv) Acetone and aniline
(v) Water and nitric acid
(vi) Diethyl ether and chloroform.

**Explanation for Negative Deviations**

When acetone and chloroform are mixed there are new attractive forces due to intermolecular hydrogen bonding. Thus the attractive forces become stronger and the escaping tendency of each liquid from the solution decreases. Therefore, the vapour pressure of the solution is less than that expected for an ideal solution.

(i) ΔmixingH is negative because energy is released due to increase in attractive forces. Therefore, dissolution process is exothermic and heating the solution will decrease solubility.

(ii)Because of the increase in the magnitude of forces of attraction in solutions, the molecules will be loosely held more tightly. Therefore, there will be decrease in volume on mixing. Thus, ΔmixingV will be negative.

## Difference between Ideal and Non-Ideal solution

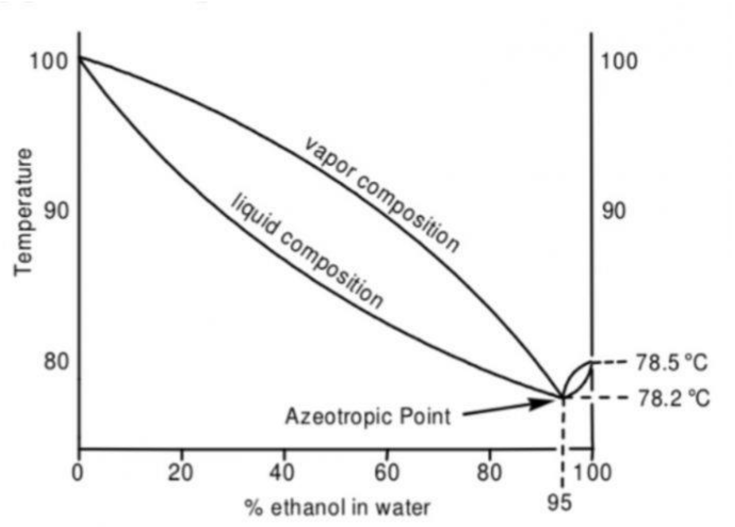
| **Solution having positive deviation** | **Solution having negative deviation** |
|---|---|
| A-B forces are less than A-A and B-B forces. | A-B forces are more than A-A and B-B forces. |
| $p_A > p_A^\circ x_A$ and $p_B > p_B^\circ x_B$ | $p_A < p_A^\circ x_A$ and $p_B < p_B^\circ x_B$ |
| ΔmixingH is positive | ΔmixingH is negative |
| Dissolution is endothermic | Dissolution is exothermic |
| Heating increases solubility | Heating decreases solubility |
| ΔmixingV will be positive. | ΔmixingV will be negative. |

**a)** Some solution exhibit very large positive deviation from Raoult’s law that there is a maximum in the vapour pressure curve which is above the vapour pressure of either pure components.

For one of the intermediate composition, the total vapour pressure of such a solution will be the highest and the boiling point will be the lowest. At this point, the composition of liquid and vapour phase is same and the liquid mixture boils at constant temperature and remains unchanged in composition. Therefore, this liquid mixture distills over as if it is a pure liquid. Solution acquires the property of boiling at constant temperature and remains unchanged in composition.

The solutions (liquid mixtures) which boil at constant temperature and can distil unchanged in composition are called azeotropes or azeotropic mixtures. Thus, the azeotropes distil over as if it were pure liquids. These types of solutions are called minimum boiling azeotropes.

**For example:** Ethanol and water form minimum boiling azeotrope. It has maximum in the vapour pressure curve and hence a minimum in the boiling point diagram. In this boiling point diagram, we indicate the composition of the vapour phase by the upper curve and composition of the liquid phase by the lower curve.



The boiling point diagram shows an azeotropic composition at $x(H_2O)=0.056$ and $x(C_2H_5OH) = 0.944$ at a temperature.of 351 K (or 78°C) which is lower than that of pure ethanol 351.5 K (or 78.5°C) and water 378 K (or 100°C).

Fractional distillation of solutions lying on either side of this azeotropic composition is capable of separating them into at best, one pure component and a azeotropic mixture having the minimum boiling point.

**b)** In the case of solutions showing negative deviations, total vapour pressure becomes less than the corresponding ideal solution of same composition. The boiling points of such solutions are increased.

For one of the intermediate composition, the total vapour pressure will be the least and the boiling point will be the highest. At this composition, the solution also boils at constant temperature without a change in composition. This is also called azeotrope.

The solutions which show negative deviations from Raoult's law are called **maximum boiling azeotropes** because they have a composition having maximum boiling point

For example: hydrochloric acid and water form maximum boiling point azeotrope at the composition $x(H_2O)=0.889$ and $x\,(HCl)=0.111$ (or 20.2% HCl) which boils at 381.6 K (or 108.6°C) which has higher than that of pure water.

Nitric acid ($HNO_3$) and water also form maximum boiling azeotrope. The azeotrope has the approximate composition 68% nitric acid and 32% water by mass with a boiling point of 393.5 K.

Thus, the azeotropes are liquid mixtures of definite composition, which boil at constant boiling point. These cannot be separated into pure components by fractional distillation.

## Colligative Properties

The properties of dilute solution which depends only on number of particles of solute (molecules or ions) present in the solution and not on their nature, are called colligative properties. The important **colligative properties** are;

1. Relative lowering of vapour pressure
2. Elevation of boiling point
3. Depression in freezing point
4. Osmotic pressure

### i. Relative Lowering of Vapour Pressure

When a non-volatile solute is added to a solvent, its vapour pressure gets **lowered**. If this pressure is divided by pressure of pure solvent, this is called **relative lowering of vapour pressure.**

According to **Raoult's law,**

$$\frac{P^\circ - P}{P^\circ} = X_A$$

where, $P^\circ$ = V.P. of pure solvent

$P^\circ - P$ = lwering in vapour pressure

$$\frac{P^\circ - P}{P^\circ} = \frac{n_A}{n_A + n_B} \ldots \left[X_A = \frac{n_A}{n_A + n_B}\right]$$

For dilute solution $n_A + n_A \approx n_A$

$$\frac{P^\circ - P}{P^\circ} = \frac{n_A}{n_B}$$

$$\frac{P^\circ - P}{P^0} = \frac{W_A}{M_A} \times \frac{M_B}{W_B}$$

where, $W_A$ = weight of solute

$W_B$ = weight of solvent

$M_A$ = molecular weight of solute
$M_B$ = molecular weight of solvent

## ii. Relative Elevation of boiling point

A liquid boils at the temperature at which its vapour pressure is equal to the atmospheric pressure. The boiling point of a solution of non-volatile solute is always higher than that of the boiling point of pure solvent in which the solution is prepared. Similar to lowering of vapour pressure, the elevation of boiling point also depends on the number of solute particles rather than their nature.

Let T° be the boiling point of pure solvent and T be the boiling point of solution. The increase in boiling point $\Delta Tb = T - T°$ is known as **elevation in boiling point**.

For dilute solutions, the $\Delta T_b$ is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m$$

$$\Delta T_b = Kbm$$

$K_b$ is molal **elevation constant** (Ebullioscopic constant). The unit of $K_b$ is K kg mol$^{-1}$.

Substituting the value of molality in above equation, we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$M_2 = \frac{K_b \times 1000 \times w_2}{\Delta T_b \times w_1}$$

Where, $w_1$ = mass of solvent, $w_2$ = mass of solute and $M_2$ = molar mass of solute

## iii. Depression in freezing point

Freezing point is the temperature at which vapour pressure of liquid phase becomes same as that of solid phase. The decrease in freezing point of a solvent on the addition of a non-volatile solute is known as **depression in freezing point**.

Let T° be the freezing point of pure solvent and T be the freezing point of solution. The decrease in freezing point $\Delta T_f = T° - T$ is known as depression in freezing point.

For dilute solutions, the $\Delta T_f$ is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_f \propto m$$

$$\Delta T_f = Kf \cdot m$$

Here $K_f$ is molal depression constant or cryoscopic constant

Substituting the value of molality in above equation, we get

$$\Delta T_f = \frac{K \times w_2 \times 1000}{M_2 \times w_1}$$

$$M_2 = \frac{K \times w_2 \times 1000}{\Delta T_f \times w_1}$$

Where, $w_1$ = mass of solvent, $w_2$ = mass of solute and $M_2$ = molar mass of solute

### iv. Osmotic pressure

**Osmosis** is the spontaneous flow of the solvent molecules from a less concentrated solution (dilute) to a more concentrated solution through a **semi-permeable membrane**. The driving force of osmosis is called **osmotic pressure**. Osmotic pressure may be defined as “the minimum excess pressure that has to be applied on the solution to prevent the osmosis".

**Osmotic pressure** of a solution ∝ molar concentration of solute in that solution

$$\pi \propto c$$

$$\pi = cRT$$

where, R = Gas constant = 0.0821 lit atm $K^{-1}$ $mole^{-1}$

T = Temperature

c = Molar concentration

$$\pi = \frac{n}{V}RT \;.....[c = \frac{n}{V}]$$

$$\pi = \frac{W_B}{M_B}\frac{RT}{V}$$

$W_B$ = wt. of solute

$M_B$ = Molar mass of solute

### van’t Hoff Factor

To calculate the extent of association or dissociation, van’t Hoff in 1886 introduced a factor ‘i’ called van’t Hoff factor. **van’t Hoff factor** ‘i’ is defined as ratio of the experimental value of colligative property to the calculated value of colligative property.

$$\text{i. e., i}\ \frac{\text{Experiment ecolligatival properties}}{\text{Calculated ecolligativ properties}}$$

## Abnormal Molar Masses

### Abnormal Molecular Masses

The accurate values of molar masses can be obtained only if the following two conditions are met.

**(i) The solutions should be dilute**

The solutions used for measuring colligative properties must not be too concentrated. In the concentrated solutions, the particles begin to interact with each other as well as with the solvent. As a result, the vapour pressure and therefore, other colligative properties depend upon the nature of the solute and not just on the number of solute particles.

**(ii) The solute must not dissociate or associate in solution**

The equations derived for measuring the colligative properties are for non-electrolyte solutes which do not undergo any dissociation or association in the solution.

Discrepancies in determination of molar mass arise when the solute dissociate or associate on dissolving in a solvent. This is because due to the association or the dissociation of the solute molecules in the solution, the number of molecules undergo a change.

The discrepancy in molar mass is called abnormal molar mass. The abnormal molar masses is due to association or dissociation of solute particles.

### Association of Solute Particles

In certain solvents, generally non-polar, the solute molecules undergo association i.e. two, three or even more molecules exist in combination with each other to form bigger molecules. For example: suppose n simple molecules combine to form an associated molecule as:

$$nA \Leftrightarrow A_n$$

Therefore, the total number of molecules in solution become less than the number of molecules of the substance added and, therefore, colligative properties will be lower. Since the colligative properties are inversely proportional to the molar mass of the solute, the molar masses in such cases will be greater than the theoretical values.

For example: In benzene solvent, both ethanoic acid (acetic acid) and benzoic acid exist as dimers as:

$$2CH3COOH \Leftrightarrow (CH3COOH)2$$

$$2C6H5COOH \Leftrightarrow (C6H5COOH)2$$

The molar masses of ethanoic acid and benzoic acid have been found to be nearly 120 and 244 which are about double than their normal values of 60 and 122. The association of solute molecules in a solution is generally due to the hydrogen bonding between these molecules.

**For example:** benzoic acid and ethanoic acid exist as dimers due to the formation of hydrogen bonds. Due to association of ethanoic acid or benzoic acid, the $\Delta Tf$ or $\Delta Tb$ value will be about half of the normal value. Therefore, the molar mass calculated on the basis of $\Delta T$ will be about twice the expected value.

## Dissociation of Solute Molecules

Molecules of certain substances (acids, bases and salts) dissociate or ionise in a solvent to give two or more particles.

For example: AB dissociates to give double number of particles as:

$$AB \Leftrightarrow A^+ + B^-$$

The total number of particles increases in solution and, therefore, the colligative properties of such solutions will be large. Since colligative properties are inversely proportional to molar mass, the observed molar mass will be less than the theoretical value.

For example, KCl dissociates to give $K^+$ and $Cl^-$ ions.

$$KCl \Leftrightarrow K^+ + Cl^-$$

If we dissolve 1 mol of KCl (74.5 g) in water, we expect 1 mol of $K^+$ and 1 mol of $Cl^-$ ions to be produced in the solution. Therefore, there would be 2 mol of particles in the solution instead of 1 mol. Consequently, the colligative properties would also be about double than expected.

For example: if we ignore interionic attraction, 1 mol of KCl in 1 kg of water would be expected to increase the boiling point by 2 X 0.52 K ($K_b$= 0.52 K$m^{-1}$) = 1.04 K.

### Van’t Hoff Factor

In 1886, Van’t Hoff introduced a factor called Van’t Hoff factor, $\mathbf{i}$ , to express the extent of association or dissociation of solutes in solution. It is the ratio of the normal and observed molar masses (or abnormal molar mass) of the solute, i.e.

$$\mathrm{i} = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

In case of association, observed molar mass being more than the normal, the factor $\mathbf{i}$ has a value less than 1.

But in case of dissociation, the Van’t Hoff factor is more than 1 because the observed molar mass has a lesser value.

In case of solutes which do not undergo any association or dissociation in a solvent, the Van't Hoff factor i will be equal to 1 because the observed and normal molar masses will be same.

Since the molar masses are inversely proportional to the colligative property. Van't Hoff factor may also be expressed as:

$$i = \frac{\text{Observed colligative property}}{\text{Normal collegative property}}$$

Relative lowering in vapour pressure = i xsolute = Δp / p°

Elevation in boiling point , Δ Tb =i Kb  m

Depression in freezing point = Δ Tf = i Kf m

Osmotic pressure π = i cRT

## Van't Hoff Factor and Extent of Dissociation or Association in an Electrolytic Solution

Van't Hoff factor can be used to calculate the extent of dissociation or association in terms of degree of dissociation or association of a substance in solution.

**(i) Degree of dissociation:** It is defined as the fraction of total substance that undergoes dissociation into ions, i.e.

**Degree of dissociation** = No. of moles of the substance dissociated / Total number of moles of the substance taken

Suppose a molecule of an electrolyte gives n ions after dissociation. Then if we start with 1 mole of the solute, and α is the degree of dissociation, then at equilibrium:

Number of moles of solute left undissociated =1-α

Number of moles of ions formed = nα

Total number of moles of particles 1-α+ nα

Van't Hoff factor, i =

Observed number of moles of solute / Normal number of moles of solute

Total number of moles at equilibrium

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

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

$$\Rightarrow \qquad \alpha = \frac{i - 1}{n - 1}$$

Knowing the value of i from observed molar mass and normal molar mass, degree of dissociation, α can be calculated.

For the electrolytes of the type AB, such as KCl, NaCl, etc,.the number of particles in solution i.e. n = 2

For the electrolytes of the type AB, like $CaCl_2$, $Ba(NO_3)2$ etc, the value of n=2, so that

$$\alpha = ( i-1 ) /2$$

(ii) Degree of association: It is defined as the fraction of total number of molecules which combine to form associated molecules, i.e.

$$\text{Degree of association} = \frac{\text{No. of moles of the substance associated}}{\text{Total number of moles of substance taken}}$$

For example: suppose n simple molecules of the solute associate to form the associated molecule A.

$$nA= \; An$$

If we start with 1 mole of A and α is the degree of association, the concentration of the species after association is

$$[An] = \alpha/n$$

$$[A] =1-\alpha$$

Total number of moles after association = $1-\alpha+ \alpha/n$

Thus, the colligative properties will correspond to (1-α+ α/n) mole particles rather than one mole of particles.

Van’t Hoff factor, i , is : Observed number of moles of solute / Normal number of moles of solute

$$= 1-\alpha + \alpha/n / 1$$

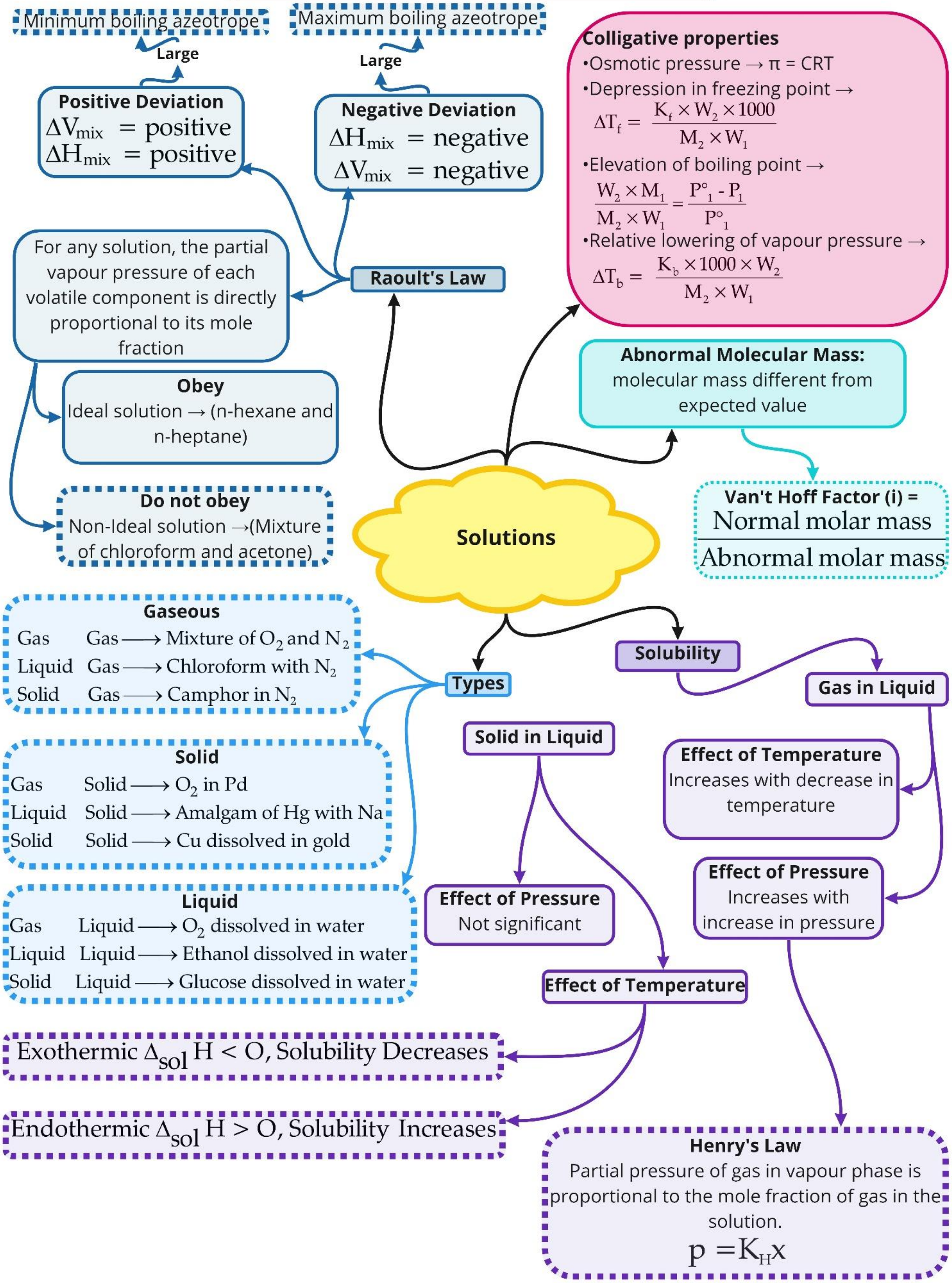
$$= 1+ \alpha (1/n -1)$$

$$\alpha =( i-1 ) /( 1/n -1)$$

$$\mathrm{I} = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

Knowing n the number of simple molecules which combine to give associated molecule, observed molar mass, degree of association(α) can be calculated.

Class : 12th Chemistry
Chapter-2 : Solutions (Part_1)



**Solutions**

**Raoult's Law**

For any solution, the partial vapour pressure of each volatile component is directly proportional to its mole fraction

**Obey**
Ideal solution → (n-hexane and n-heptane)

**Do not obey**
Non-Ideal solution →(Mixture of chloroform and acetone)

**Positive Deviation**
$\Delta V_{mix} = \text{positive}$
$\Delta H_{mix} = \text{positive}$

Large → Minimum boiling azeotrope

**Negative Deviation**
$\Delta H_{mix} = \text{negative}$
$\Delta V_{mix} = \text{negative}$

Large → Maximum boiling azeotrope

**Colligative properties**

- Osmotic pressure → $\pi = CRT$
- Depression in freezing point →
  $$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$
- Elevation of boiling point →
  $$\frac{W_2 \times M_1}{M_2 \times W_1} = \frac{P^\circ_1 - P_1}{P^\circ_1}$$
- Relative lowering of vapour pressure →
  $$\Delta T_b = \frac{K_b \times 1000 \times W_2}{M_2 \times W_1}$$

**Abnormal Molecular Mass:**
molecular mass different from expected value

**Van't Hoff Factor (i) =**
$$\frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

**Types**

**Gaseous**
Gas $\quad$ Gas $\longrightarrow$ Mixture of $O_2$ and $N_2$
Liquid $\quad$ Gas $\longrightarrow$ Chloroform with $N_2$
Solid $\quad$ Gas $\longrightarrow$ Camphor in $N_2$

**Solid**
Gas $\quad$ Solid $\longrightarrow$ $O_2$ in Pd
Liquid $\quad$ Solid $\longrightarrow$ Amalgam of Hg with Na
Solid $\quad$ Solid $\longrightarrow$ Cu dissolved in gold

**Liquid**
Gas $\quad$ Liquid $\longrightarrow$ $O_2$ dissolved in water
Liquid $\quad$ Liquid $\longrightarrow$ Ethanol dissolved in water
Solid $\quad$ Liquid $\longrightarrow$ Glucose dissolved in water

**Solubility**

**Solid in Liquid**

**Effect of Pressure**
Not significant

**Effect of Temperature**

Exothermic $\Delta_{sol} H < O$, Solubility Decreases

Endothermic $\Delta_{sol} H > O$, Solubility Increases

**Gas in Liquid**

**Effect of Temperature**
Increases with decrease in temperature

**Effect of Pressure**
Increases with increase in pressure

**Henry's Law**
Partial pressure of gas in vapour phase is proportional to the mole fraction of gas in the solution.
$$p = K_H x$$

Class : 12th Chemistry
Chapter-2 : Solutions (Part_2)

## Solutions

**Parts per million : For trace quantities**

$$\frac{\text{No. of parts of components} \times 10^6}{\text{Total no. parts of components of solution}}$$

**Normality:** Number of gram equivalents of the solute dissolved in one litre of solution

$$\frac{\text{No. of gram equivalentof solute} \times 100}{\text{Volume of solution}}$$

↓

Gram Equivalents of solute

$$= \frac{\text{Mass of solute}}{\text{Equivalent weight}}$$

↓

$$\text{Equivalent weight} = \frac{\text{Molecular mass}}{\text{Valency}}$$

**Mass by volume percentage (w/v)**

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

**Mass percentage w/w**

$$\frac{\text{Mass of component in solution}}{\text{Total mass of solution}} \times 100$$

**Volume percentage v/v**

$$\frac{\text{Volume of component}}{\text{Total volume of solution}} \times 100$$

**Mole fraction**

$$\frac{\text{No. of moles of component}}{\text{Total No. of moles of all components}}$$

**Molality:** Number of moles of solute per kilogram of the solvent

$$\frac{\text{No. of moles of solute} \times 100}{\text{Mass of solvent}}$$

**Molarity:** Number of moles of solute in 1L solution

$$\frac{\text{No. of moles of solute} \times 100}{\text{Volume of solution}}$$

# Important Questions

## Multiple Choice questions-

Question 1. Which of the following units is useful in relating concentration of solution with its vapour pressure?

(a) mole fraction

(b) parts per million

(c) mass percentage

(d) molality

Question 2. On dissolving sugar in water at room temperature, solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid?

(a) Sugar crystals in cold water.

(b) Sugar crystals in hot water.

(c) Powdered sugar in cold water.

(d) Powdered sugar in hot water.

Question 3. At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is

(a) less than the rate of crystallisation

(b) greater than the rate of crystallisation

(c) equal to the rate of crystallisation

(d) zero

Question 4. A beaker contains a solution of substance 'A'. Precipitation of substance 'A' takes place when small amount of 'A' is added to the solution. The solution is ………………

(a) saturated

(b) supersaturated

(c) unsaturated

(d) concentrated

Question 5. Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does not depend upon .

(a) temperature

(b) nature of solute

(c) pressure

(d) nature of solvent

Question 6. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to

(a) low temperature

(b) low atmospheric pressure

(c) high atmospheric pressure

(d) both low temperature and high atmospheric pressure

Question 7. Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult’s law?

(a) Methanol and acetone.

(b) Chloroform and acetone.

(c) Nitric acid and water.

(d) Phenol and aniline.

Question 8. Colligative properties depend on

(a) the nature of the solute particles dissolved in solution.

(b) the number of solute particles in solution.

(c) the physical properties of the solute particles dissolved in solution.

(d) the nature of solvent particles.

Question 9.Which of the following aqueous solutions should have the highest boiling point?

(o) 1.0 M NaOH

(b) 1.0 M $Na_2SO_4$

(c) 1.0 M $NH_4NO_3$

(d) 1.0 M $KNO_3$

Question 10. The unit of ebullioscopic constant is

(a) K kg $mol^{-1}$ or K $(molality)^{-1}$

(b) mol kg $K^{-1}$ or $K^{-1}$ (molality)

(c) kg $mol^{-1}$ $K^{-1}$ or $K^{-1}$ $(molality)^{-1}$

(d) K mol $kg^{-1}$ or K (molality)

Question 11.In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M $MgCl_2$ solution is ………..

(a) the same

(b) about twice

(c) about three times

(d) about six times

Question 12.An unripe mango placed in a concentrated salt solution to prepare pickle shrivels because ………..

(a) it gains water due to osmosis.

(b) it loses water due to reverse osmosis.

(c) it gains water due to reverse osmosis.

(d) it loses water due to osmosis.

Question 13. At a given temperature, osmotic pressure of a concentrated solution of a substance

(a) is higher than that of a dilute solution.

(b) is lower than that of a dilute solution.

(c) is same as that of a dilute solution.

(d) cannot be compared with osmotic pressure of dilute solution.

Question 14. Which of the following statements is false?

(a) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.

(b) The osmotic pressure of a solution is given by the equation $\pi = cRT$ (where c is the molarity of the solution).

(c) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is $BaC_{l2}$ > KCl > $CH_3COOH$ > sucrose.

(d) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution.

Question 15.he values of Van't Hoff factors for KCl, NaCl and $K_2SO_4$, respectively, are

(a) 2, 2 and 2

(b) 2, 2 and 3

(c) 1,1 and 2

(d) 1, 1 and 1

**Very Short Question:**

Question 1. Define the term – solubility?

Question 2. What is the effect of pressure on solubility of a gas?

Question 3. State Henry's Law.

Question 4. State Raoult's Law.

Question 5. What are the factors on which vapour pressure depends?

Question 6. The vapour pressure of solvent gets lowered, when a non- volatile solute is added to it. Why?

Question 7. Name two ways by which vapour pressure of a liquid can be lowered.

Question 8. Define solution?

Question 9. Define the following terms:

(a) Molality

(b) Molarity

Question 10. How does change in temperature changes the molarity and molality values?

### Short Questions:

Question 1 Find the molality and molarity of a 15% solution of $H_2SO_4$ when its density is

a) 1.10 glcm$^3$ & molar mass = 98 amu.

Question 2. Calculate the mole fraction of ethanol and water in a sample of rectified spirit which contains 46% ethanol by mass?

Question 3. Calculate the % composition in terms of mass of a solution obtained by mixing 300g of a 25% & 400 g of a 40% solution by mass?

Question 4. One litre of sea water weight 1030g and contains about $6 \times 10^{-3} g$ of dissolved $O_2$ Calculate the concentration of dissolved oxygen in ppm?

Question 5. The density of 85% phosphoric acid is. $1.70\, g/cm^3$ What is the volume of a solution that contains 17g of phosphoric acid?

Question 6. Define the term azeotrope?

Question 7. Obtain a relationship between relative lowering of vapour pressure and mole fraction of solute?

Question 8. Draw the graphs of both deviations from ideal behaviours?

Question 9. A weak electrolyte AB in 5% dissociated in aqueous solution? What is the freezing point of a 0.10 molar aqueous solution of AB? $K_f$ = 1.86 deg/molal?

Question 10. Henry's law constant for the molality of methane in benzene at 298 K is . $4.27 \times 105\,\text{mm Hg}$ Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

## Long Questions:

**Question 1.**

The vapour pressure of $CS_2$ $500^0 C$ at is 854 mm Hg .A solution of 2.0g sulphur in 100g of has a vapour pressure $CS_2$ of 848.9 mm Hg .Calculate the formula of sulphur molecule

**Question 2**. Calculate the mass percentage of benzene ($C_6H_6$) and carbon tetrachloride ($CCl_4$) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

**Question 3**. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

**Question 4**. Calculate the molarity of each of the following $CO(NO_3)_2$ $6H_2O$ solutions: (a) 30 g of . in 4.3 L of solution (b) 30 mL of 0.5 M $H_2SO_4$ diluted to 500mL.

**Question 5**.Calculate (a)molality (b)molarity and (c)mole fraction of KI if the density of 20% (mass/mass) aqueous KI $1.202\,g\,ml^{-1}$ is

## Assertion and Reason Questions:

**1.** In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

**Assertion:** Camphor is used as a solvent in the determination of molecular masses of naphthalene, anthracene, etc.

**Reason:** Camphor has high molal elevation constant.

**2.** In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

**Assertion:** Reverse osmosis is used in the desalination of sea water.

**Reason:** When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane.

## Case Study Questions:

**1.** Read the passage given below and answer the following questions:

The solubility of gases increases with increase of pressure. William Henry made a systematic investigation of the solubility of a gas in a liquid. According to Henry's law "the mass of a gas dissolved per unit volume of the solvent at constant temperature is directly proportional to the pressure of the gas in equilibrium with the solution". Dalton during the same period also concluded independently that the solubility of a gas in a ti quid solution depends upon the partial pressure of the gas. If we use the mole fraction of gas in the solution as a measure of its solubility, then Henry's law can be modified as "the partial pressure of the gas in the vapour phase is directly proportional to the mole fraction of the gas in the solution"

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Henry's law constant for the solubility of methane in benzene at 298K is $4.27 \times 10^5$mm Hg. The solubility of methane in benzene at 298K under 760mm Hg is:

a) $4.27 \times 10^{-5}$
b) $1.78 \times 10^{-3}$
c) $4.27 \times 10^{-3}$
d) $1.78 \times 10^{-5}$

(ii) The partial pressure of ethane over a saturated solution containing $6.56 \times 10^{-2}$g of ethane is I bar. If the solution contains $5.00 \times 10^{-2}$g of ethane then what will be the partial pressure (in bar) of the gas?

a) 0.762
b) 1.312
c) 3.81
d) 5.0

(iii) $K_H$ (K bar) values for $Ar_{(g)}$, $CO_{2(g)}$, $HCHO_{(g)}$ and $CH_{4(g)}$ are 40.39, 1.67, $1.83 \times 10^{-5}$ and 0.413 respectively. Arrange these gases in the order of their increasing solubility. Arrange these gases in the order of their increasing solubility.

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

(iv) When a gas is bubbled through water at 298K, a very dilute solution of the gas is obtained. Henry's law constant for the gas at 298K is 150 kbar. If the gas exerts a partial pressure of 2 bar, the number of millimoles of the gas dissolved in IL of water is:

a) 0.55
b) 0.87
c) 0.37
d) 0.66

(v) Which of the following statements is correct?

a) $K_H$ increases with increase of temperature.
b) $K_H$ decreases with increase of temperature.
c) $K_H$ remains constant with increase of temperature.
d) $K_H$ first increases then decreases, with increase of temperature.

**2.** Read the passage given below and answer the following questions

Few colligative properties are:

1. Relative lowering of vapour pressure: depends only on molar concentration of solute (mole fraction) and independent of its nature.
2. Depression in freezing point: it is proportional to the molal concentration of solution.
3. Elevation of boiling point: it is proportional to the molal concentration of solute.
4. Osmotic pressure: it is proportional to the molar concentration of solute

A solution of glucose is prepared with 0.052 g at glucose in 80.2 g of water. ($KJ = 1.86K\ kg\ mol^{-1}$ and $K_b = 5.2K\ kg\ mol^{-1}$)

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Molality of the given solution is.

a) 0.0052m

b) 0.0036m
c) 0.0006m
d) 1.29m

(ii) Boiling point for the solution will be.

a) 373.05K
b) 373.15K
c) 373.02K
d) 373.02K

(iii)The depression in freezing point of solution will be.

a) 0.0187K
b) 0.035K
c) 0.082K
d) 0.067K

(iv)Mole fraction of glucose in the given solution is.

a) $6.28 \times 10^{-5}$
b) $6.28 \times 10^{-4}$
c) 0.00625
d) 0.00028

(v) If same amount of sucrose ($C_{12}H_{22}O_{11}$) is taken instead of glucose, then.

a) Elevation in boiling point will be higher.
b) Depression in freezing point will be higher.
c) Depression in freezing point will be lower.
d) Both (a) and (b).

## Answers key

### MCQ answers:

1. Answer: (a) mole fraction

2. Answer: (d) Powdered sugar in hot water.

3. Answer: (c) equal to the rate of crystallisation

4. Answer: (b) supersaturated

5. Answer: (c) pressure

6. Answer: (b) low atmospheric pressure

7. Answer: (a) Methanol and acetone.

8. Answer: (b) the number of solute particles in solution.

9. Answer: (b) 1.0 M $Na_2SO_4$

10. Answer: (a) K kg $mol^{-1}$ or K $(molality)^{-1}$

11. Answer: (c) about three times

12. Answer: (d) it loses water due to osmosis.

13. Answer: (a) is higher than that of a dilute solution.

14. Answer: (a) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.

15. Answer: (b) 2, 2 and 3

### Very Short Answers:

1. The maximum amount of a substance that can be dissolved in a specified amount of solvent is called its solubility.

2. The solubility of a gas increases with increases of pressure.

3. Answer: Henry's Law states that at a constant temperature the solubility of a gas in a liquid is directly proportional to the pressure of the gas.

4. Answer: Raoult's Law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

5. Answer: The factors on which vapour pressure depends are –
   1) Temperature of the liquid. 2) Nature of the liquid.

6. Answer: When a non-volatile solute is added to a solvent, the surface area for escape of solvent molecules decreases and vapour pressure gets lowered.

7. Answer: The two ways by which vapour pressure can be lowered are –

   1) By decreasing the temperature.

2) By adding a non- volatile solute.

8. Solutions are homogeneous mixtures of two or more than two components..

9. (a) Molality is defined as the number of moles of the solute per kilogram of solvent.

$$\text{Molality (m)} = \frac{\text{Moles of solutes}}{\text{Mass of solvent in Kg}}$$

(b) Molarity (M) = Number of moles of solute dissolved in one litre of solution.

$$\text{Molarity (M)} = \frac{\text{No. of Moles of solute}}{\text{Volume of solution in litre}}$$

10. As the temperature increases, volume increases and molarity decreases whereas molality does not change with any change in temperature.

## Short Answers:

**1. Answer**

Volume = mass/density

$$= 100\ g / 1.10\ g/cm^3 = 90.9\ cm^3$$

$$\text{Molarity} = \frac{\text{no. of moles of } H_2SO_4}{\text{volume of solution}} \times 1000$$

$$= \frac{(15/98)}{90.9} \times 1000 = 1.68\ \text{m}$$

.

$$\text{Molality} = \frac{\text{no. of moles of solute}}{\text{mass of solvent in kg}}$$

$$\frac{(15/98)}{85g} \times 1000$$

= 1.8 M.

**2. Answer:**

Mass of ethanol = 46g

Mass of water = 100 – 46 = 54g

$$X_A = \frac{X_A}{X_A + X_B}$$

Mole fraction of ethanol,

$$= \frac{\frac{46}{46}}{\frac{46}{46}+\frac{54}{18}} = \frac{1}{1+3} = \frac{1}{4} = 0.25.$$

Mole fraction of water = 1-0.25 = 0.75

Mole fraction of water = 1-0.25 = 0.75

**3. Answer:**

mass of solute in 400g of 40%

$$= \frac{40}{100} \times 400 = 160\text{g}$$

Total mass of solute = 160+75 = 235g

Total mass of solution = 400+300 = 700g

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

$$= \frac{235}{700} \times 100 = 33.57\%$$

Mass % of solvent = 100 – 33.57 = 66.43%

**4. Answer:**

mass of $O_2 = 6 \times 10^{-3} g$

ppm of $O_2$ in 1030 g sea water = $\frac{\text{mass of } o_2}{\text{mass of sea water}} \times 10^6$

$$= \frac{6 \times 10^{-3}}{1030} \times 10^6 = 5.8 \text{ ppm.}$$

**5. Answer :**

Ans. 85g phosphoric acid is present in 100g of solution.

17g of phosphoric acid is present in

$$\frac{100}{85} \times 17 = 20\text{g of soution}$$

Volume of 17g of 85% acid = $\frac{mass}{density}$

$$= \frac{20g}{1.70 g/cm^3} = 11.8\ \text{cm}^3$$

**6. Answer**

A solution at certain concentration when continues to boil at constant temperature without change in its composition in solution & in vapour phase is called an azeotrope.

**7. Answer:**

According to Raoult's Law –

$$P_1 = x_1 p_1^0$$

$$\Delta P = P_1^0 - P = P_1^0 - P_1^0 X_1$$

$$= \Delta P_1 = P_1^0 (1 - X_1)$$

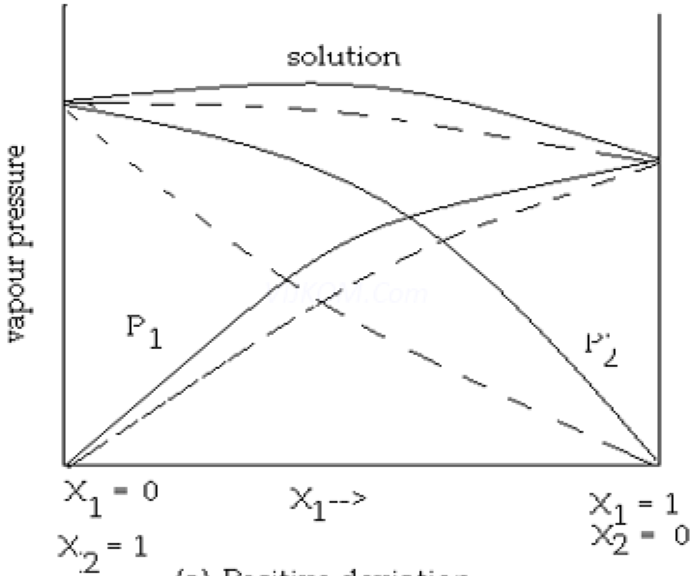
$$\Delta P_1 = P_1^0 X_2 (X_1 + X_2 = 1)$$

$$\frac{\Delta P_1}{P_1^0} = \text{X}_2$$

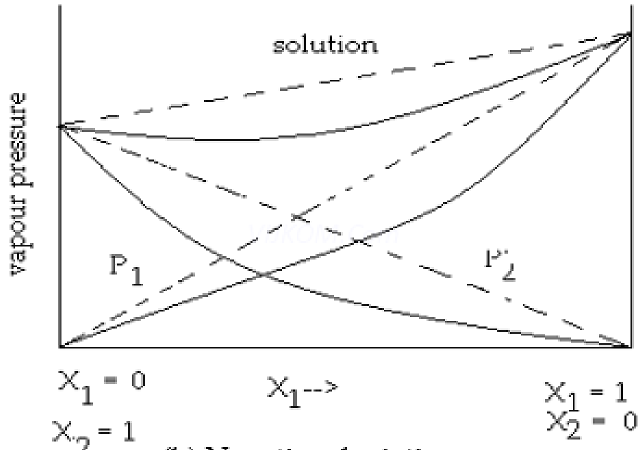
$$= \frac{P_1^0 - P_1}{P_1^0} = \text{X}_2$$

Relative lowering of vapour pressure.

**8. Answer:**



(a) Positive deviation.



(b) Negative deviation

**9. Answer :**

Degree of dissociation $\alpha$ of AB = $\frac{5}{100} = 0.05$

AB $\rightarrow$ A$^+$ + B$^-$

M 0 0

No. of moles dissolved

No. of moles after dissociations

m (1-$\alpha$) m$\alpha$ m$\alpha$

0.1 (1 – 0.05) $0.1\times0.05$ $0.1\times0.0$

Total moles = 0.1(1–0.05) + $(0.1\times0.05)$ + $(.1\times0.05)$

= 0.095 + 0.005 + 0.005 = 0.105m

$\Delta T_f = K_f .m$

$= 1.86 \times 0.105$

= 0.1953 deg.

$T_f = 0^0C - 0.1953 = 0.1953^0C$

**10.Answer :**

*p* = 760 mm Hg

$k_H = 4.27 \times 105\,\text{mm Hg}$

According to Henry's law,

$p = k_H x$

$x = \frac{p}{k_H}$

$= \frac{760\,\text{mm Hg}}{4.27\times10^5\,\text{mm Hg}}$

$= 177.99\times10^{-5}$

= $178 \times 10^{-5}$ (approximately)

Hence, the mole fraction of methane in benzene is $178 \times 10^{-5}$.

## Long Answers:

1. **Answer:**

$P_A^o$ = 854 mm $P_A = 848.m$, $W_B = 2.0g$,

$W_A = 100\ g\ M_B = ?$

$M_A = 12 + 2(32) = 76\ g/mol\ /CS^2)$

$$\frac{P_A^0 - P_A}{P_A^0} = X_B = \frac{W_B}{M_B} / \frac{W_A}{M_A}$$

= $M_B = W_B \times \frac{W_A}{M_A} \times \frac{P_A^0}{P_A - P_A}$

= $2 \times \frac{100}{76} \times \frac{854}{854 - 848.9}$

= 254.5 g/mol.

Let the formula = Sx

$X \times 32 = 254.5\ g/mol$

X= $\frac{254.5}{32}$

=7.95

=8.

= Formula = $S_8$

**2. Answer:**

Mass percentage $C_6H_6 = \frac{\text{Mass of } C_6H_6}{\text{Total mass of the solution}} \times 100\%$ of

$= \frac{\text{Mass of}}{\text{Mass of } C_6H_6 +}$

$= \frac{22}{22 + 122} \times 100\%$

=15.28%

Mass percentage of $CCl_4$ = $\frac{\text{Mass of } CCl_4}{\text{Total mass of the solution}} \times 100\%$

$$= \frac{\text{Mass of } CCl_4}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4}$$

$$= \frac{122}{22+122} \times 100\%$$

= 84.72%

Alternatively,

Mass percentage of $CCl_4$ = (100 – 15.28) %

= 84.72%

**3. Answer:**

Let the total mass of the solution be 100 g and the mass of benzene be 30g.

∴ Mass of carbon tetrachloride = (100 – 30) g

= 70 g

Molar mass of benzene ($C_6H_6$) = (6 × 12 + 6 ×) $g\ mol^{-1}$

= 78 $g\ mol^{-1}$

∴ Number of moles of $C_6H_6 = \frac{30}{78} mol$

= 0.3846 mol

Molar mass of carbon tetrachloride ($CCl_4$) = 1 × 12 + 4 × 355

= 154 $g\ mol^{-1}$

**∴Number of moles** $CCl_4 = \frac{70}{154} mol$ **of**

**= 0.4545 mol**

**Thus, the mole fraction of** $C_6H_6$ **is given as:**

$$\frac{\text{Number of moles of } C_6H_6}{\text{Number of moles of } C_6H_6 + \text{Number of moles of } CCl_4}$$

$$= \frac{0.3846}{0.3846 + 0.4545}$$

**= 0.458**

**4. Answer:**

Molarity is given by:

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume solution in litre}}$$

**(a)** Molar mass of $CO(NO_3)_2.6H_2O$ 59 + 2 (14 + 3× 16) + 6×18

= 291 $\text{g mol}^{-1}$

Therefore, Moles of $CO(NO_3)_2.6H_2O = \frac{30}{291}\text{mol}$

= 0.103 mol

Therefore, $= \frac{0.103\text{mol}}{4.3\text{L}}$ molarity

= 0.023 M

**(b)** Number of moles present in 1000 mL of 0.5 $H_2SO_4 = 0.5\text{ mol}$ M

∴Number of moles present in 30 mL of 0.5 M $H_2SO_4 = \frac{0.5 \times 30}{1000}\text{ mol}$

= 0.015 mol

Therefore, molarity $= \frac{0.015}{0.5\text{L}}\text{mol}$ = 0.03 M

**5. Answer:**

**(a)** Molar mass of KI = 39 + 127 = 166 $\text{g mol}^{-1}$

20% (mass/mass) aqueous solution of KI means 20 g of KI is present in 100 g of solution.

That is,

20 g of KI is present in (100 – 20) g of water = 80 g of water

Therefore, molality of the solution= $\frac{\text{Moles of KI}}{\text{Mass of water in kg}}$

$$\frac{\frac{20}{166}}{0.08}\text{m}$$

= 1.506 m

= 1.51 m (approximately)

**(b)** It is given that the density of the solution = $1.202\,\text{g ml}^{-1}$

Therefore, Volume of 100 g solution = $\dfrac{\text{Mass}}{\text{Density}}$

$$\frac{100\text{g}}{1.202\,\text{g ml}^{-1}}$$

= 83.19 mL

= $83.19 \times 10^{-3}\text{L}$

Therefore, molarity of the solution = $\dfrac{\frac{20}{166}\text{mol}}{83.19\times10^{-3}\,\text{L}}$

**(c)** Moles of KI = $\dfrac{20}{166} = 0.12\text{mol}$

Moles of water = $\dfrac{80}{18} = 4.44\text{mol}$

Therefore, mole fraction of KI = $\dfrac{\text{Moles of KI}}{\text{Moles of KI} + \text{Moles of water}}$

$= \dfrac{0.12}{0.12+4.44}$

= 0.0263

## Assertion and Reason Answers:

**1.** (c) Assertion is correct statement but reason is wrong statement.

**Explanation:**

Camphor has high molal depression constant.

**2.** (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

**Explanation:**

If a pressure larger than the osmotic pressure is applied to the solution side, the pure solvent flows out of the solution to the solvent through semi-permeable membrane and this phenomenon is called reverse osmosis.

## Case Study Answers:

**1. Answer :**

i. (b) $1.78 \times 10^{-3}$

**Explanation:**

$$K_H = 4.17 \times 10^5 \text{mm HG}$$

$$p = 760 \text{mm Hg}$$

According to Henry's law, $P = K_H \times X_{CH_4}$

$$X_{CH_4} = \frac{P}{K_H} = \frac{760}{4.27 \times 10^5} = 1.78 \times 10^{-3}$$

ii. (a) 0.762

**Explanation:**

According to Henry's law, $m = K_H \times p$

$6.56 \times 10^{-2} = K_H \times 1$

For another case, $5 \times 10^{-2} = 6.56 \times 10^{-2} \times p$

$$p = \frac{5 \times 10^{-2}}{6.56 \times 10^{-2}} = 0.762 \text{ bar}$$

iii. (c) $Ar < CO_2 < CH_4 < HCHO$

**Explanation:**

Higher the value of $K_H$ at a given pressure, the lower is the solubility of the gas.

iv. (c) 0.37

**Explanation:**

The mole fraction of the gas in solution,

$$x = \frac{p}{K_H} = \frac{1}{150 \times 10^3}$$

If n is the number of moles of gas in a solution of I L of water containing 55.5 mol then,

$$x = \frac{n}{n+55.5} \text{ or, } \frac{n}{55.5} = \frac{1}{150 \times 10^3}$$

$$[n + 55.5 \approx 55.5, \text{as n is very small}]$$

$$n = \frac{55.5}{150} \times 10^{-3} = 0.37 \text{ millimoles}$$

v. (a) $K_H$ increases with increase of temperature.

**2. Answer :**

i. (b) 0.0036m

**Explanation:**

$$m = \frac{0.052}{180} \times \frac{1000}{80.2} = 0.0036$$

ii. (c) 373.02K

**Explanation:**

$$\Delta T_b = k_b \times m = 5.2 \times 0.0036 = 0.0187 \text{ K}$$

$T_b$ = 373 + 0.0187 = 373.0187 K ≈ 373.02 K

iii. (d) 0.067 K

**Explanation:**

$$\Delta T_f = k_f \times m = 1.86 \times 0.0036 = 0.067 \text{ K}$$

iv. (a) $6.28 \times 10^{-5}$

**Explanation:**

Moles of water $\frac{80.2}{18} = 4.455$

Mole fraction of glucose $= \frac{0.00028}{4.45+0.00028} = 6.28 \times 10^{-5}$,

V. (c) Depression in freezing point will be lower.

**Explanation:**

Depression in freezing point or elevation in boiling point is proportional to molarity, which is proportional to number of moles. For same amount, higher the molar mass of solute, lower will be number of moles. Hence, lower will be the colligative property.