

## LIQUID SOLUTIONS

### SOLUTION

A homogeneous mixture of two or more pure substances whose composition may be altered within certain limits is termed as solution.



#### Characteristics of Solution

- (i) It is homogeneous in nature, yet retaining the properties of its constituents.
- (ii) It is made of two parts i.e. a solute and a solvent.



**Which component to take as solute and which component to take as solvent depends on physical state of the components.**

- (iii) The component which has the same physical state in pure form as the solution is called solvent and the other is called solute. Example, in case of solution of sugar and water, sugar is the solute and water is solvent.
- (iv) If both the components have same state as the solution, the one component which is in excess is called solvent and the other is called solute. Example, alcohol in water, benzene in toluene etc.

#### Types of Solution

S.No.	Solvent	Solute	Examples
1.	Gas	Gas	Mixture of gases, air.
2.	Gas	Liquid	Water vapour in air, mist.
3.	Gas	Solid	Sublimation of a solid into a gas, smoke storms.
4.	Liquid	Gas	CO <sub>2</sub> gas dissolve in water (aerated drink), soda water.
5.	Liquid	Liquid	Mixture of miscible liquids e.g. alcohol in water.
6.	Liquid	Solid	Salt in water, sugar in water.
7.	Solid	Gas	Adsorption of gases over metals, hydrogen over palladium.
8.	Solid	Liquid	Mercury in zinc, mercury in gold i.e. all amalgams.
9.	Solid	Solid	Homogeneous mixture of two or more metals (i.e. alloys) e.g. copper In gold, zinc In copper.



**Which of the above types can never have a heterogeneous mixture.**

## METHODS OF EXPRESSING THE CONCENTRATION OF A SOLUTION

There are many ways of expressing the concentration of a solution. These methods are as follows-



**Students should memories all the formulas and should be comfortable in converting one concentration term to another.**



**Comment which of the following concentration terms are temperature dependent and which are temperature independent.**

### (i) Mass percentage :

It may be defined as the number of parts by mass of solute per hundred parts by mass of solution.



**For example, a 5% (by mass) solution of sugar in water means that 100 g of solution contain 5 g of sugar.**

$$\text{Mass Percentage} = \frac{\text{Mass of any component}}{\text{total mass}} \times 100$$

### (ii) Volume percentage :

It may be defined as the number of parts by volume of solute per hundred parts by volume of solution.



**For example, a 25% (by volume) solution of ethyl alcohol means that 100 cm<sup>3</sup>. of the solution contain 25 cm<sup>3</sup> of ethyl alcohol and 75 cm<sup>3</sup> of water.**

$$\text{Volume percentage} = \frac{\text{Volume of component}}{\text{total volume of solution}} \times 100$$

### (iii) Mass fraction :

If W<sub>A</sub> is the mass of component A and W<sub>B</sub> the mass of component B in the solution, then the mass fraction of component A and B is written as

$$\text{Mass fraction of A} = \frac{W_A}{W_A + W_B}$$

$$\text{Mass fraction of B} = \frac{W_B}{W_A + W_B}$$

### (iv) Mole fraction

Mole fraction may be defined as the ratio of the number of moles of one component to the total number of moles of all the components (i.e. solute and solvent) present in the solution.

Let us suppose that a solution contains the components A and B and suppose that a gram of A and b gram of B are present in it. Let the molecular masses of A and B are M<sub>A</sub> and M<sub>B</sub> respectively.

$$\text{Then number of moles of A are given by } n_A = \frac{a}{M_A}$$

and number of moles of B are given by  $n_B = \frac{b}{M_B}$

Total number of moles of A and B =  $n_A + n_B$

Mole fraction of A,  $X_A = \frac{n_A}{n_A + n_B}$

Mole fraction of B,  $X_B = \frac{n_B}{n_A + n_B}$

**Sum of mole fractions of all components is always one.**



$$\text{i.e. } X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

So if mole fraction of one component of a binary solution is known say  $X_B$ , then the mole fraction of  $X_A = 1 - X_B$ .



**It may be noted that the mole fraction is always independent of the temperature.**

#### (v) Mole percent

Mole percent is the number of moles of a component in 100 mole of the solute and solvent.

Mole percent = Mole fraction  $\times 100$

Example. for a solution containing 8 moles  $\text{NH}_3$  and 12 moles of  $\text{H}_2\text{O}$ .

$$\text{Mole fraction of } \text{NH}_3, X_{\text{NH}_3} = \frac{8 \text{ mole}}{12 \text{ moles} + 8 \text{ moles}} = \frac{2}{5}$$

$$\text{Mole percent of } \text{NH}_3 = \frac{2}{5} \times 100 = 40 \text{ mole \%}$$

#### (vi) Parts per million (ppm)

When a solute is present in trace amounts, its concentration is expressed in parts per million. It may be defined as the number of parts by mass of solute per million parts by mass of the solution.



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

#### (vii) Molarity (M)

Molarity of a solution is defined as the number of moles of the solute dissolved per litre of the solution. It is represented by capital M. Mathematically,

$$\text{Molarity (M)} = \frac{\text{Mass of the solution in gram per litre}}{\text{Molecular mass of the solute}}$$

A solution having molarity "one" is called molar solution.



**It may be remembered that both normality as well as molarity of a solution changes with change in temperature.**

(viii) **Molality (m) -**

Molality of a solution may be defined as the number of moles of the solute dissolved in 1000 gm (1 kg) of the solvent. It is represented by small 'm'. Mathematically

$$\text{Molality (m)} = \frac{\text{Mass of the solute in gram per kg of solvent}}{\text{Molecular mass of the solute}}$$

A solution containing one mole of solute per 1000 gm of solvent (1 kg) has molality equal to one and is called molal solution. Molality is expressed in units of moles per kilogram ( $\text{mol kg}^{-1}$ ).



**The molality of a solution does not change with temperature.**

(ix) **Normality :**

Normality of a solution is defined as the number of gram equivalent of the solute dissolved per litre of the solution. It is represented by N. Mathematically,

$$\text{Normality N} = \frac{\text{Mass of solute in gram per litre}}{\text{Equivalent mass of the solute}}$$

A solution having normality equal to one is called "normal solution". Such a solution contains one gram equivalent of solute per litre of solution. A seminormal solution contains 0.5 gram equivalent of solute. A decinormal solution contains 0.1 gram equivalent and a centinormal solution contains 0.01 gram equivalent of solute per litre of solution.

$$\text{or Normality} = \frac{\text{Mass of the solution} \times 1000}{\text{Equivalent mass of the solute} \times V}$$

Where V is the volume in milliliter.

(x) **Formality (F) :**

It may be defined as the number of gram formula masses of the ionic solutes dissolved per litre of the solution. Mathematically

$$\text{Formality (F)} = \frac{\text{Mass of the ionic in gram per litre}}{\text{Formula mass of the solute}}$$

Commonly, the term formality is used to express the concentration of the ionic solids which do not exist as molecule but as network of ions.

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***Illustration***

1. A storage battery contains a solution of  $\text{H}_2\text{SO}_4$  30% by weight. Find out  
 (i) Molality                   (ii) Molarity                   (iii) Normality                   (iv) Mole fraction of  $\text{H}_2\text{SO}_4$   
 (Given density of solution = 1.2 gm/cm<sup>3</sup>)

Sol. 30% by weight  $\Rightarrow W_{\text{solute}} = 30 \text{ gm}$ ,  $W_{\text{solution}} = 100 \text{ gm}$ ,  $W_{\text{solvent}} = 70 \text{ gm}$

$$V_{\text{solution}} = \frac{100}{1.2} \text{ mL}$$

$$n_{\text{solution}} = \frac{30}{98} = 0.306 \quad n_{\text{solvent}} = \frac{70}{18} = 3.889$$

$$(i) \quad \text{Molality} = \frac{n_{\text{solute}} \times 1000}{W_{\text{solvent}}} = \frac{0.306 \times 1000}{70} = 4.37 \text{ m}$$

$$(ii) \quad \text{Molarity} = \frac{n_{\text{solute}} \times 1000}{V_{\text{solution}}} = \frac{0.306 \times 1000}{\frac{100}{1.2}} = 3.67 \text{ M}$$

$$(iii) \quad \text{Normality} = \frac{W_{\text{solute}} \times 1000}{E_{\text{solute}} \times V_{\text{solution}}} = \frac{30 \times 1000}{49 \times \frac{100}{1.2}} = 7.34 \text{ N}$$

Alternatively

$$\begin{aligned} \text{Normality} &= n\text{-factor} \times \text{Molarity} \\ &= 2 \times 3.67 = 7.34 \end{aligned}$$

$$(iv) \quad x_{\text{H}_2\text{SO}_4} = \frac{x_{\text{H}_2\text{SO}_4}}{n_{\text{H}_2\text{SO}_4} + n_{\text{H}_2\text{O}}} = \frac{0.306}{0.306 + 3.889} = 0.07$$

***Exercise***

1. In a solution mole fraction of solute is 0.2. Find out molality of solution. (Given molar mass of solute 40 gm mole<sup>-1</sup>)  
 Ans. 13.89 m
2. 14.2 gm  $\text{Na}_2\text{SO}_4$  is dissolved in 400 mL water. Find out (i) formality (ii) Normality of solution.  
 Ans. 0.25, 0.75

***SOLUBILITY OF GASES***

We are familiar that gases are completely miscible with each other. Gases also dissolve in liquids and solids. For example, soda-water contains carbon dioxide dissolved in water under high pressure. Oxygen is sufficiently soluble in water to allow survival of aquatic life in lakes, rivers and oceans. An example of dissolution of a gas in a solid is the solubility of hydrogen gas in palladium.

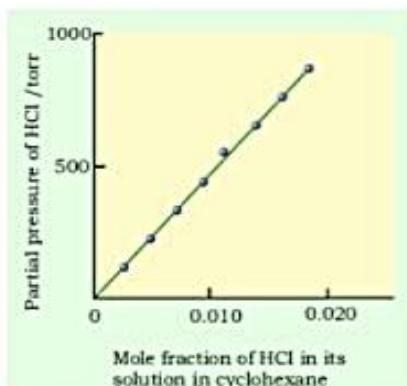
The solubility of a gas in a liquid is determined by several factors. In addition to the nature of the gas and the liquid, solubility of the gas depends on the temperature and pressure of the system. The solubility of a gas in a liquid is governed by Henry's Law which states that the solubility of a gas in a liquid is directly proportional to the pressure of the gas.

Dalton, a contemporary of Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of the partial pressure of the gas. If we use the mole fraction of the gas in the solution as a measure of its solubility, then:



**Mole fraction of the gas in a solution is proportional to the partial pressure of the gas. Or, partial pressure of the gas in solution =  $K_H \times$  mole fraction of the gas in solution. Here  $K_H$  is Henry's law constant or  $p = K_H \times x$ .**

If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in figure.



**Figure : Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant ( $K_H$ )**



Different gases have different  $K_H$  values at the same temperature. This suggests that  $K_H$  is a function of the nature of the gas.

It is obvious that the higher the value of  $K_H$  at a given pressure, the lower is the solubility of the gas in the liquid. It has been observed that  $K_H$  value for both  $N_2$  and  $O_2$  increases with increase of temperature indicating that solubility of gases decreases with increase of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than warm waters.

Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

- To increase the solubility of  $CO_2$  in soft drinks and soda water, the bottle is sealed under high pressure.
- To minimize the painful effects accompanying the decompression of deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.
- In lungs, where oxygen is present in air with high partial pressure, haemoglobin combines with oxygen to form oxyhaemoglobin. In tissues where partial pressure of oxygen is low, oxyhaemoglobin releases oxygen for utilization in cellular activities.

### **Limitations of Henry's Law : For Henry's law to be applicable**

- (i) Gas should not react with solvent.
- (ii) Gas should not associate or dissociate in solution.
- (iii) This law is not applicable for highly concentrated solutions.

### **Illustration**

1. If  $N_2$  gas is bubbled through water at 293K, how many millimoles of  $N_2$  gas would dissolve in 1 litre of water. Assume that  $N_2$  exerts a partial pressure of 0.987 bar. Given that Henry's law constant for  $N_2$  at 293 K is 76.48 k bar.

**Sol.** The solubility of gas is related to its mole fraction in the aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus,

$$x_{N_2} = \frac{P_{N_2}}{K_H} = \frac{0.987 \text{ bar}}{76480 \text{ bar}} = 1.29 \times 10^{-5}$$

As 1 litre water contains 55.5 mol of it, therefore, if n represents number of moles of  $N_2$  in solution,

$$x_{N_2} = \frac{n \text{ mol}}{n \text{ mol} + 55.5 \text{ mol}} \approx \frac{n}{55.5} = 1.29 \times 10^{-5}$$

$$\text{Thus, } n = 1.29 \times 10^{-5} \times 55.5 \text{ mol} = 7.16 \times 10^{-4} \text{ mol}$$

$$= 7.16 \times 10^{-4} \text{ mol} \times \frac{1000 \text{ m mol}}{1 \text{ mol}} = 0.716 \text{ m mol}$$

### **Exercise**

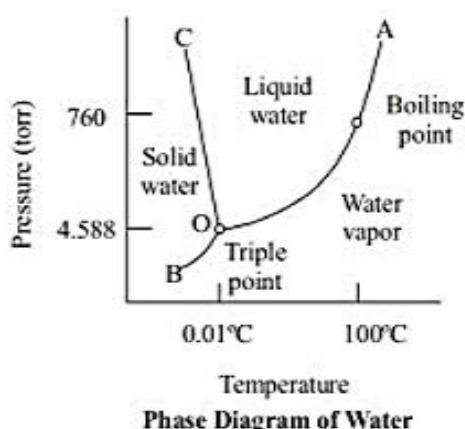
1. Henry's law constant for oxygen and nitrogen dissolved in water at 298K are  $2.0 \times 10^9 \text{ Pa}$  and  $5.0 \times 10^9 \text{ Pa}$ , respectively. A sample of water at a temperature just above 273 K was equilibrated with air (20% oxygen and 80% nitrogen) at 1 atm. The dissolved gas separated from a sample of this water and then dried. Determine the composition of this gas.

**Ans.** Amount percent of  $O_2$  = 38.27%, Amount percent of  $N_2$  = 61.73%

### **Phase Diagram of water**

The lines represent simultaneous values of pressure and temperature at which two phases may be present at equilibrium. At the temperatures and pressures that lie on the line OA, liquid water and its vapor are at equilibrium. Along the line OB, ice and its vapor are at equilibrium, while the sets of temperature and pressure at which both ice and liquid water are in equilibrium lie along OC. Only at the pressure and temperature corresponding to the triple point ( $0.01^\circ\text{C}$ , 4.588 torr) are ice, water and water vapor simultaneously present at equilibrium. The areas between the curves represent temperatures and pressures at which only one phase can exist.

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## VAPOUR PRESSURE OF SOLUTION AND RAOUULTS LAW

### (i) Vapour Pressure

If a sample of water in its liquid phase is placed in an empty container, some of it will vaporize to form gaseous water. This change is called evaporation. We can write an equation for evaporation occurring spontaneously as if it were a chemical equation :



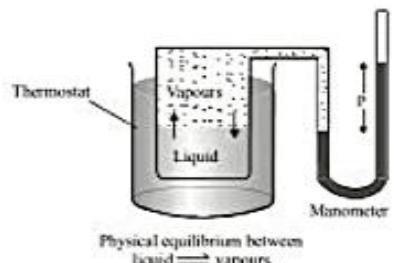
$$K_p = P_{\text{H}_2\text{O}}$$

where

$K_p$  = equilibrium constant

$P_{\text{H}_2\text{O}}$  = vapour pressure of  $\text{H}_2\text{O}(g)$

The pressure exerted by the vapour (molecules in the vapour phase) over the surface of the liquid at the equilibrium at given temperature is called the vapour pressure of the liquid.



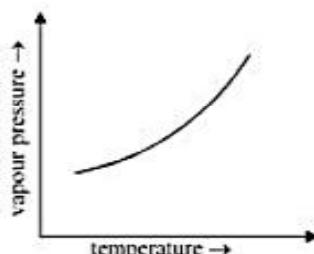
Is vapour pressure dependent on surface area and shape of the container?



### Factors affecting vapour pressure

(a) **Temperature** : Vapour pressure  $\propto$  Temperature

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called its *boiling point*.



Can you guess what will be the equation relating vapour pressure and temperature.

**(b) Nature of liquid:**

Vapour pressure of liquid  $\propto \frac{1}{\text{The strength of intermolecular forces acting between molecules}}$

For example,  $\text{CCl}_4$  has higher vapour pressure because of the weak intermolecular forces acting between its molecules than water which has stronger intermolecular forces acting between water molecules of volatile liquid has lower boiling point than a non-volatile liquid.

- (ii) Raoult's Law for volatile solute :** For a two component solution A (volatile) and B (volatile) the vapour pressure of solution is given by



Vapour pressure of solution = Vapour pressure of solvent in solution + Vapour pressure of solute.

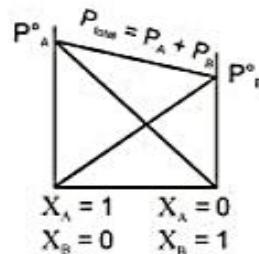
According to Raoult's Law partial pressure of a component is equal to its mole fraction in solution multiplied with partial pressure in pure state

$$\text{Thus } P_A = P_A^0 X_A$$

$P_A^0$  = vapour pressure in pure state of A

$X_A$  = Mole fraction of A in solution

$P_A$  = Partial pressure of A in solution



$$\text{Total vapour pressure of solution } P = P_A^0 X_A + P_B^0 X_B$$

**Illustration**

1. At  $25^\circ\text{C}$ , the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of  $\text{CH}_3\text{OH}$  in a solution in which the (partial) vapor pressure of  $\text{CH}_3\text{OH}$  is 23.0 torr at  $25^\circ\text{C}$ ?

Sol. 
$$X_{\text{CH}_3\text{OH}} = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CH}_3\text{OH}}^0} = \frac{23}{96} = 0.24$$

**Exercise**

1. The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.

Ans. 66.13 mm Hg

- (iii) Relative Lowering of Vapour Pressure :** When a small amount of a **non-volatile solute** is added to the liquid (solvent). It is found that the vapour pressure of the solution is less than that of the pure solvent. This is due to the fact that the solute particles occupy a certain surface area and evaporation takes place from the surface only. The particles of the solvent will have a less tendency to change

into vapour i.e. the vapour pressure of the solution will be less than that of the pure solvent and it is termed as **lowering of vapour pressure**.

For a solution of non-volatile solute with volatile solvent.

$$P = P_A X_A \quad P = \text{vapour pressure of solution}$$

$$P_A = P_A^0 X_A \quad P_A = \text{vapour pressure of solvent}$$

If mole fraction of solute is  $X_B$ , then  $X_A$  = mole fraction of solvent and  $P_A^0$  = vapour pressure of pure solvent.

$$X_A + X_B = 1$$

$$P_A = P_A^0 (1-X_B) = P_A^0 - P_A^0 X_B$$

$$X_B = \frac{P_A^0 - P_A}{P_A^0}$$



$(P_A^0 - P_A)$  is the **lowering of vapour pressure** whereas  $\left( \frac{P_A^0 - P_A}{P_A^0} \right)$  is called **relative lowering of vapour pressure**.

$$\text{Mole fraction of solute} = \frac{\text{Vapour pressure of pure solvent} - \text{Vapour pressure of solution}}{\text{vapour pressure of solvent}}$$

### Illustration

1. The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?

Ans. 0.25

$$\text{Sol. } X_B = \frac{P_A^0 - P_{\text{sol}}}{P_A^0} = \frac{0.80 - 0.60}{0.80} = 0.25$$

### Exercise

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

Ans.  $P_A^{\circ} = 213.33$  torr,  $P_B^{\circ} = 960.0$  torr

2. The vapour pressure of pure water at  $25^{\circ}\text{C}$  is 23.76 torr. The vapour pressure of a solution containing 5.40 g of a nonvolatile substance in 90.0 g water is 23.32 torr. Compute the molecular weight of the solute.

Ans. 57.24 g/mol

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

Ans. 111.1g, 18.52 molal



So Raoult's law can also be defined as "For a solution containing non-volatile solute, at a particular temperature. The relative lowering of vapour pressure is equal to mole fraction of the solute".



Vapour pressure of solutions having non volatile solute will always be less than that of solvent, however vapour pressure of solutions with volatile solute may be more or less than that of pure solvent.

#### (iv) Types of Solutions

**(a) Ideal Solution :** An ideal solution may be defined as the one which obeys Raoult's law over all concentration ranges at a given temperature. The total vapour pressure of an ideal solution containing liquids A and B is given by the following equation.

$$P = P_A + P_B = P_A^o X_A + P_B^o X_B$$

In an ideal solution of two components A and B, all attractive forces between A and B molecules or between A and A molecules or between B and B molecules (A-B, A-A and B-B) must be identical so that the escaping tendency of an A or B molecule is independent of whether it is surrounded by A molecules, B, molecules or varying proportions of A and B molecules. The escaping tendency of pure liquid A in solution remains the same. Similarly the escaping tendency of B remains the same. Liquids form ideal solution only when they have nearly same molecular size and related constitution so that they have similar molecular environment in the pure state as well as in solution. A perfect ideal solution is rare but many liquids form nearly ideal solution. Liquid heptane and hexane form an ideal solution because the interaction between a hexane molecule and another heptane molecule is the same as the interaction between two heptane molecules other examples of ideal solutions are:



benzene + toluene,  
ethyl bromide + ethyl iodide;  
ethyl alcohol + methyl alcohol

chlorobenzene + bromobenzene;  
n-butyl chloride + n-butyl bromide

#### Conditions for forming ideal solution:

Two liquids on mixing form an ideal solution only when

1. both have similar structures and polarity so that they have similar molecular environment.
2. both have similar molecular sizes.
3. both have identical intermolecular forces.

**(b) Non-ideal solutions :** Solutions which do not obey Raoult's law over all concentration ranges at constant temperature are called non-ideal solutions.

### Distinction between ideal & non ideal solutions

S.No.	Ideal solution	Non Ideal solution
1.	They obey Raoult's Law	They do not obey Raoult's Law
2.	$\Delta H_{\text{mixing}} = 0 \Rightarrow$ no heat is absorbed or released during dissolution	$\Delta H_{\text{mixing}} \neq 0 \Rightarrow$ heat is absorbed or released during dissolution
3.	$\Delta V_{\text{mixing}} = 0 \Rightarrow$ the total volume of the solution is equal to the sum of the volume of the pure liquids mixed to form the solution	$\Delta V_{\text{mixing}} \neq 0 \Rightarrow$ the total volume of the solution is not equal to the sum of the volume of the pure liquids mixed to form the solution.
4.	In ideal solution $P_A = P_A^{\circ} X_A$	In non ideal solution $P_A \neq P_A^{\circ} X_A$
5.	Components of ideal solution can be separated in pure form by fractional distillation	Components of non ideal solution can not be separated in pure form by fractional distillation

### Types of non-ideal solutions

- (I) Non ideal solutions showing positive deviation  
 (II) Non ideal solutions showing negative deviation.

#### (I) Non ideal solutions showing positive deviation

**Condition for forming non-ideal solution showing positive deviation from Raoult's law.**

Two liquids A and B on mixing form this type of solution when

1. A—B attractive force should be weaker than A—A and B—B attractive forces.
2. 'A' and 'B' have different shape, size and character.
3. 'A' and 'B' escape easily showing higher vapour pressure than the expected value.

#### Example :

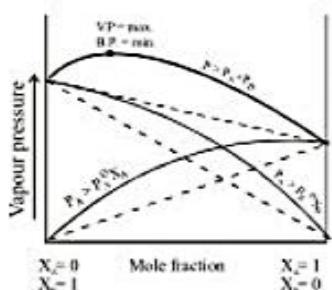


acetone + ethanol  
 water + ethanol;  
 acetone + benzene;

acetone +  $CS_2$   
 $CCl_4$  + toluene;  
 $CCl_4$  +  $CH_3OH$ ;

water + methanol;  
 $CCl_4$  +  $CHCl_3$ ;  
 cyclohexane + ethanol

#### Graphical representation of vapour pressure of non-ideal solution showing positive deviation



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## (II) Non ideal solutions showing negative deviation.

Condition for forming non-ideal solution showing negative deviation from Raoult's law.

Two liquids A and B on mixing form this type of solution when

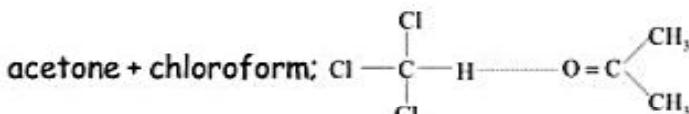
1. A—B attractive force should be greater than A—A and B—B attractive forces.
2. 'A' and 'B' have different shape, size and character
3. Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.

**Example:**

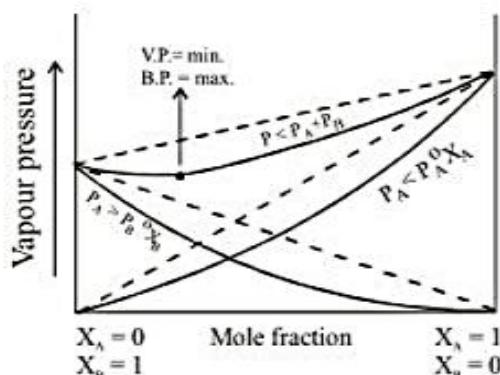


acetone + aniline;  
chloroform + diethyl ether,  
chloroform + benzene  
water + HCl

$\text{CH}_3\text{OH} + \text{CH}_3\text{COOH};$   
 $\text{acetic acid} + \text{pyridine};$   
 $\text{H}_2\text{O} + \text{HNO}_3;$



Graphical representation of vapour of non-ideal solution showing negative deviation



**Distinction between non ideal solutions showing positive deviation & negative deviation**

S.No.	Showing positive deviation	Showing negative deviation
1.	$\Delta H_{\text{mix}} > 0$ . (endothermic dissolution i.e. heat is absorbed.)	$\Delta H_{\text{mix}} < 0$ . (Exothermic dissolution i.e. heat is evolved.)
2.	$\Delta V_{\text{mix}} > 0$ . (Volume is increased after dissolution)	$\Delta V_{\text{mix}} < 0$ . (Volume is decreased during dissolution)
3.	$p_A > p_A^° X_A$ ; $p_B > p_B^° X_B$ , $\therefore p_A + p_B > p_A^° X_A + p_B^° X_B$	$p_A < p_A^° X_A$ ; $p_B < p_B^° X_B$ , $\therefore p_A + p_B < p_A^° X_A + p_B^° X_B$

### (v) Azeotropes



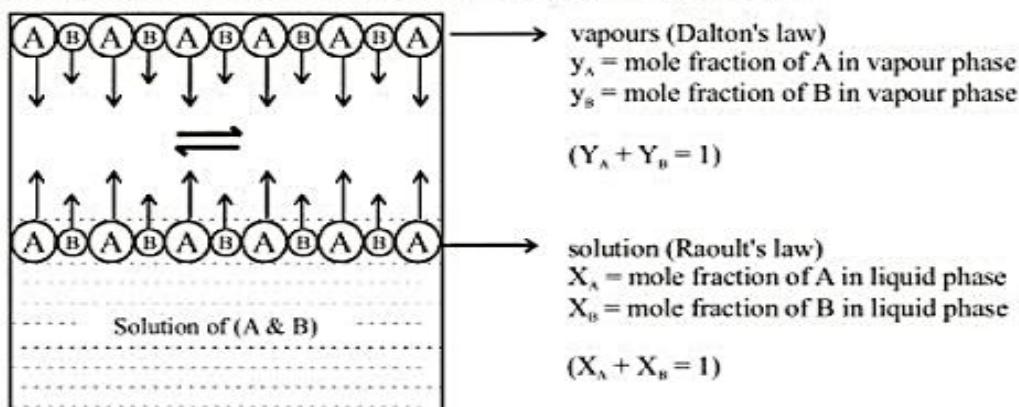
The non-ideal solution showing large deviations from Raoult's law can not be purified by distillation. A solution at certain composition which continues to boil at constant temperature without change in the composition of the solution.

- This mixture is called **Azeotrope or Constant boiling mixture**. Azeotropes are of two types:
- (a) **Azeotropes with Maximum vapour pressure and Minimum Boiling point :** When liquid in a solution do not have great chemical affinity for each other (+ve deviation from ideality) their higher escape tendencies increase the vapour pressure much more than expected on the basis of Raoult's law. In many cases, the deviations are so extreme as to lead to a maximum in the curve. The point of maximum vapour pressure means that the boiling point at this composition will be minimum and constant.
- (b) **Azeotropes with Minimum vapour pressure and Maximum Boiling Point :** When liquids in solution show -ve deviation from ideality, their escape tendencies and hence the vapour pressure decreases than expected on the basis of Raoult's law. In many cases, the maximum in the temperature composition curve is obtained. The point of minimum vapour pressure in the curve means that the boiling point of this composition will be maximum and constant.

(vi) **Determination of composition in vapour phase**

**Dalton's Law v/s Raoult's Law:**

The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures. Let the mole fractions of vapours A and B be  $y_A$  and  $y_B$  respectively. Let  $p_A$  and  $p_B$  be the partial pressure of vapours A and B respectively and total pressure P.



$$\text{From Raoult's law } P = P_A^o X_A + P_B^o X_B \\ P_A = P_A^o X_A \text{ and } P_B = P_B^o X_B$$

From Dalton's law,

$$\text{Partial pressure} = \text{Mole fraction} \times \text{Total pressure}$$

$$\text{For A } P_A = y_A \times P = P_A^o X_A$$

$$\Rightarrow y_A = \frac{P_A^o X_A}{P} \quad \dots\dots(1)$$

Similarly

$$\Rightarrow y_B = \frac{P_B^o X_B}{P} \quad \dots\dots(2)$$

Above formula is used for calculation of mole fraction of B in vapour phase

$$\text{on adding } X_A + X_B = \frac{P \times y_A}{P_A^o} + \frac{P \times y_B}{P_B^o} = 1$$

$$\Rightarrow \frac{1}{P} = \frac{y_A}{P_A^o} + \frac{y_B}{P_B^o} \quad \dots\dots(3)$$

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Above formula is used to calculate total vapour pressure when mole fractions are given in vapour phase



$P = P_A^o X_A + P_B^o X_B \Rightarrow$  This formula is used to calculate total pressure when mole fraction are given in liquid phase

$\frac{1}{P} = \frac{y_A}{P_A^o} + \frac{y_B}{P_B^o} \Rightarrow$  This formula is used to calculate total pressure when mole fraction are given in vapour phase



Thus, in case of ideal solution the vapour phase is richer with more volatile component i.e., the one having relatively greater vapour pressure.

### Illustration

- The vapour pressures of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour.

Sol. No. of moles of  $C_2H_5OH = \frac{60}{46} = 1.304$ , No. of moles of  $CH_3OH = \frac{40}{32} = 1.25$

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

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

$$\text{Partial pressure of ethyl alcohol} = X_A \cdot P_A^o = 0.5107 \times 44.5 = 22.73 \text{ mm Hg}$$

$$\text{Partial pressure of methyl alcohol} = X_B \cdot P_B^o = 0.4893 \times 88.7 = 43.40 \text{ mm Hg}$$

$$\text{Total vapour pressure of solution} = 22.73 + 43.40 = 66.13 \text{ mm Hg}$$

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

### Exercise

- At 90°C, the vapour pressure of toluene is 400 torr and that of  $\sigma$ -xylene is 150 torr. What is the composition of the liquid mixture that boils at 90°C, when the pressure is 0.50 atm? What is the composition of vapour produced?

Ans. 92 mol% toluene; 96.8 mol % toluene

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

(A)  $Y_A < Y_B$       (B)  $X_A > X_B$       (C)  $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$       (D)  $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

Ans. (C)

## COLLIGATIVE PROPERTIES



The properties of dilute solutions containing nonvolatile solute, which depends upon relative number of solute and solvent particles but do not depend upon their nature are called colligative properties.

Some of the colligative properties are  
 (i) Relative lowering of vapour pressure  
 (ii) Elevation in boiling point  
 (iii) Depression in freezing point; and  
 (iv) Osmotic pressure.

**Factors that Affect the Colligative Property :** The number of solute particles in solution. To be more accurate, the colligative property depends upon the fraction of solute and solvent particles in solution.

- (1) Nature of the solvent
- (2) Independent of the nature of the solute
- (3) Extent of association and dissociation of solute particles in solution.

### (i) Relative Lowering of Vapour Pressure

As shown earlier the mathematical expression for relative lowering of vapour pressure is as follows

$$\frac{\Delta P}{P_A^0} = X_B = \text{mole fraction of solute}$$

$$\Delta P = P_A^0 - P_A = \text{lowering of vapour pressure}$$

$$P_A = \text{vapour pressure of pure solvent}$$

Molecular mass of non-volatile substance can be determined from relative lowering of vapour pressure

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

For dilute solution  $W_B / M_B < W_A / M_A$  and hence  $W_B / M_B$  may be neglected in the denominator. So

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{W_B / M_B}{W_A / M_A} = \frac{W_B}{W_A} \times \frac{M_A}{M_B} \quad \text{or} \quad M_B = \frac{W_B / M_A}{W_A} \left( \frac{P_A^0}{P_A^0 - P_A} \right)$$

### Illustration

1. One mole of a non-volatile solute is dissolved in two moles of water. The vapour pressure of the solution relative to that of water is

- (1) 2/3
- (2) 1/3
- (3) 1/2
- (4) 3/2

Sol.  $\frac{P_{\text{solvent}}^0 - P_{\text{solution}}}{P_{\text{solvent}}^0} = \frac{1}{1+2} = \frac{1}{3}$  (mole fraction of solute in solution) Or  $\frac{P_{\text{solution}}}{P_{\text{solvent}}^0} = 1 - \frac{1}{3} = \frac{2}{3}$

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**Exercise**

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

**Ans.** 17.38

2. Pressure over ideal binary liquid mixture containing 10 moles each of liquid A and B is gradually decreased isothermally. If  $P_A^o = 200$  mm Hg and  $P_B^o = 100$  mm Hg, find the pressure at which half of the liquid is converted into vapour.

(A) 150 mm Hg      (B) 166.5 mm Hg      (C) 133 mm Hg      (D) 141.4 mm Hg

**Ans.** (D)

(ii) **Elevation in Boiling Point**

The boiling points elevates when a non-volatile solute is added to a volatile solvent. Which occurs due to lowering of vapour pressure.

The boiling point of a liquid may be defined as the temperature at which its vapour pressure becomes equal to atmospheric pressure.

So when a non-volatile solute is added to a volatile solvent results lowering of vapour pressure and consequent elevation of boiling point

where

$$\Delta T_b = T_b - T_b^o$$

$\Delta T_b$  = elevation in B.P.

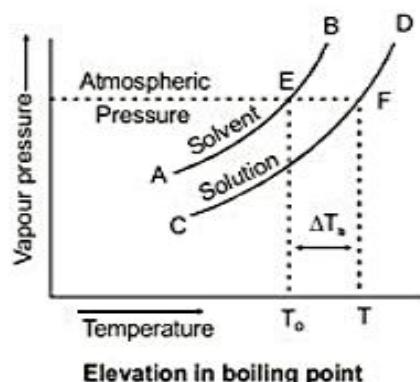
$\Delta P$  = lowering of V.P.

$X_B$  = mole fraction of solute

$K$  = elevation constant

$T_b^o$  = boiling point of solvent

$T_b$  = boiling point of solution



It is found that elevation of boiling point is directly proportional to the number of moles of the solute in given amount of the solvent(m).

$$\Delta T_b \propto m$$

$$\Delta T_b \propto K_b m$$

Where 'm' is the molality of solution.

Where  $K_b$  is ebullioscopic or boiling point elevation constant. When molality of the solution is equal to one. Then

$$\Delta T_b = K_b$$

Hence molal elevation constant of the solvent may be defined as the elevation in its boiling point when one mole of non-volatile solute is dissolved per kg (1000 gm) of solvent. The unit of  $K_b$  are  $K \text{ kg mol}^{-1}$ .

$$\text{Because molality of solution } m = \frac{W_B}{M_B} \cdot \frac{1000}{W_A}$$

$$\text{So } \Delta T_b = K_b \frac{W_B}{M_B} \cdot \frac{1000}{W_A}$$

$$M_B = \frac{1000 \times K_b \times W_B}{\Delta T_b \times W_A}$$

Where  $W_A$  = mass of solvent,  $W_B$  = mass of solute,  
 $M_A$  = Molar mass of solvent,  $M_B$  = Molar mass of solute.

### Determination of $K_b$ of solvent :



$$K_b = \frac{RT_b^2}{1000L_v} \quad \dots\dots(3)$$

where R is molar gas constant,  $T_b$  is the boiling point of the solvent on Kelvin scale and  $L_v$  the latent heat of vaporization of solvent in calories per gram.

For water  $K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515 \text{ K-kg/mol}$



If energy is taken in joule then use  $R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$   
Energy is taken in calorie then use  $R = 2 \text{ cal K}^{-1} \text{ mole}^{-1}$

### Illustration

1. An aqueous solution of glucose boils at  $100.01^\circ\text{C}$ . The molal elevation constant for water is  $0.5 \text{ K mol}^{-1} \text{ Kg}$ . The number of molecules of glucose in the solution containing 100 g of water is  
(A)  $6.023 \times 10^{23}$       (B)  $6.023 \times 10^{22}$       (C)  $12.046 \times 10^{20}$       (D)  $12.046 \times 10^{23}$

Ans. (C)

Sol.  $\Delta T_b = K_b \cdot m$       Or       $m = \frac{\Delta T_b}{K_b} = \frac{0.01}{0.5} = .02 \text{ mole Kg}^{-1}$  of water

So, the number of moles of glucose in 100 g of water

$$= \frac{0.02 \times 100}{1000} = 0.002 \text{ moles of glucose} \quad = 0.002 \times 6.023 \times 10^{23} = 2 \times 6.023 \times 10^{20}$$

### Exercise

1. Estimate the boiling point of a solution of 25.0g of urea  $\text{NH}_2\text{CONH}_2$  plus 25.0g of thiourea  $\text{NH}_2\text{CSNH}_2$ , in 500g of chloroform,  $\text{CHCl}_3$ . The boiling point of pure chloroform is  $61.2^\circ\text{C}$ ,  $K_b$  of chloroform =  $3.63 \text{ Km}^{-1}$ .

Ans.  $66.645^\circ\text{C}$

2. Calculate the molal elevation constant,  $K_b$  for water and the boiling point of 0.1 molal urea solution. Latent heat of vaporisation of water is  $9.72 \text{ kcal mol}^{-1}$  at  $373.15 \text{ K}$ .

Ans.  $K_b = 0.512 \text{ kg mol K}^{-1}$ ,  $T_b = 373.20 \text{ K}$

### (iii) Depression in Freezing Point

The freezing point of a pure liquid is fixed. If a non-volatile solute is dissolved in a liquid the freezing point of the solution is lowered. The freezing point is that temperature at which the solvent has the same vapour pressure in two phases liquid solution and solid solvent. Since the solvent vapour pressure in solution is depressed. Its vapour pressure will become equal to that of the solid solvent at a lower temperature

$$\Delta T_f = T^{\circ}_f - T_f$$

It is found that depression in freezing point is directly proportional to the number of moles of the solute in given amount of the solvent(m).

Hence

$$\Delta T_f \propto m$$

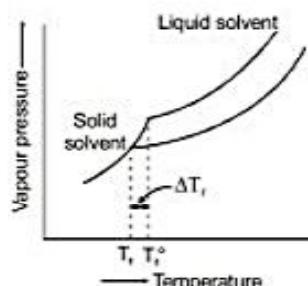
$$\Delta T_f = K_f m$$

Where m = molality of the solution.

$K_f$  = molal depression constant

When molarity (m) of the solution is one, then

$$\Delta T_f = K_f$$



Hence molal depression constant or molal cryoscopic constant may be defined as "the depression in freezing point when one mole of non-volatile solute is dissolved per kilogram (1000 gm) of solvent" and molar depression constant is defined as "the depression in freezing point when one mole of non-volatile solute is dissolved per litre (1000 ml) of solvent."

The molecular mass of the non-volatile solute may be calculated by the use of following mathematical equation

$$M_B = \frac{K_f \times W_B \times 1000}{W_A \times \Delta T_f}$$

Where  $W_A$  = mass of solvent,  $W_B$  = mass of solute,

$M_A$  = Molar mass of solvent,  $M_B$  = Molar mass of solute.

### Determination of $K_f$ of solvent

$K_f$  is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.



$$K_f = \frac{RT_f^2}{1000L_f} \quad \dots\dots(3)$$

where  $T_f$  is the freezing point of solvent in absolute scale and  $L_f$  the latent heat of fusion in calories per gram of the solvent. For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86 \text{ K-kg/mole}$$



If energy is taken in joule then use  $R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$   
Energy is taken in calorie then use  $R = 2 \text{ cal K}^{-1} \text{ mole}^{-1}$

### $K_b$ , $K_f$ for various Solvents

Solvent	B.P.	$K_b$	F.P.	$K_f$
Acetic acid	118.1°C	2.93	17°C	3.9
Benzene	80.2°C	2.53	5.4°C	5.13
Water	100°C	0.53	0°C	1.86

#### Antifreeze solutions -



Water is used in radiators of vehicles as cooling liquid. If the vehicle is to be used at high altitudes where temperature is sub-zero, water would freeze in radiators. To avoid this problem, a solution of ethylene glycol in water is used in radiators which will lower the freezing point lower than zero.

#### Illustration

1. What is the percent by mass of iodine needed to reduce the freezing point of benzene to 3.5°C? The freezing point and cryoscopic constant of pure benzene are 5.5°C and 5.12 K/m respectively.

Sol.  $\Delta T_f = T_f^0 - T_f = K_f \cdot m$   
 $5.5^\circ\text{C} - 3.5^\circ\text{C} = 5.12 \times m$

$$m = \frac{2}{5.12} = 0.39 \text{ molal}$$

$$\therefore \text{Mass of iodine needed for } 1000\text{g of benzene} = m \times \text{molecular mass of iodine } I_2 \\ = 0.39 \text{ mol/kg} \times 254 \text{ g/mol} = 99.06 \text{ g/kg}$$

$$\therefore 1000\text{g} + 99.06\text{g solution contains } 99.06\text{g } I_2$$

$$100\text{g solution contains } \frac{99.06\text{g} \times 100}{1099.06\text{g}} = 9.01\%$$

#### Exercise

1. The elements X and Y form compounds having molecular formula  $XY_2$  and  $XY_4$ . When dissolved in 20 gm of benzene, 1 gm  $XY_2$  lowers the freezing point by 2.3°, whereas 1 gm of  $XY_4$  lowers the freezing point by 1.3°C. The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.

Ans.  $x = 25.6, y = 42.6$

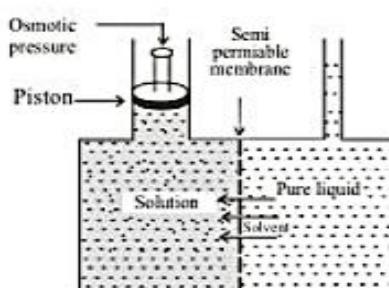
2. Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to  $-9.3^\circ\text{C}$ . ( $K_f$  for water =  $1.86 \text{ K mol}^{-1} \text{ kg}$ )

Ans. 38.71 g

#### (iv) Osmotic Pressure

(a) **Osmosis :** Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to a concentrated solution) is termed as osmosis.

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**(b) Osmotic Pressure :**

When a solution is separated from the pure solvent with the help of a semipermeable membrane. There occurs the flow of solvent molecules from the pure solvent to the solution side. The flow of solvent molecules from a region of higher concentration of solvent to the region of lower concentration of solvent is termed as the phenomenon of osmosis. This also happens when two solution of different concentrations are separated by a semipermeable membrane.

As a result of osmosis a pressure is developed which is termed as osmotic pressure. It is defined in various methods.

- (1) The excess hydrostatic pressure which builds up as a result of osmosis is called osmotic pressure.
- (2) The excess pressure that must be applied to the solution side to prevent the passage of solvent into it through a semipermeable membrane.
- (3) Osmotic pressure of a solution is equal to the negative pressure which must be applied to the solvent in order to just stop the osmosis.
- (4) The osmotic pressure of a solution may be defined as the extra pressure which should be applied to the solution to increase the 'chemical potential of solvent in solution equal to the chemical potential of the pure solvent at the same temperature.

**(c) Theory of Dilute Solutions :** The osmotic pressure of a dilute solution was the same as the solute would have exerted if it were a gas at the same temperature as of the solution and occupied a volume equal to that of the solution. This generalization is known as **Van't Hoff theory of dilute solutions**.

The osmotic pressure is a colligative property. So the osmotic pressure is related to the number of moles of the solute by the following relation

$$\pi V = nRT$$

$$\pi = \frac{n}{V} RT \quad (\therefore \frac{n}{V} = C)$$

$$\pi = CRT$$

Here C = concentration of solution in moles per litre;

R = solution constant;

T = temperature in Kelvin degree;

n = number of moles of solute; and

V = volume of solution.

This equation is called **Van't Hoff's equation**.

**(d) Determination of molecular mass from osmotic pressure :** The molecular mass of a substance i.e. solute can be calculated by applying the following formula

$$M = \frac{WRT}{\pi V}$$

Accurate molecular mass will only be obtained under following conditions

- (i) The solute must be non-volatile;
- (ii) The solution must be dilute; and
- (iii) The solute should not undergo dissociation or association in the solution.

**Solution constant R -** The solution constant R has the same significance and value as the gas constant. i.e.

$$\begin{aligned} R &= 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \times 10^{-7} \text{ erg K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1} \end{aligned}$$

#### **(e) Type of solutions :**



- (I) Isotonic solution :** The two solutions having equal osmotic pressure are termed as isotonic solution.
- (II) Hypertonic solution :** A solution having higher osmotic pressure than some other solution is said to be called hypertonic solution.
- (III) Hypotonic solution :** A solution having a lower osmotic pressure relative to some other solution is called hypotonic solution.

#### **(f) Semipermeable membrane :**

A membrane which allows the passage of solvent molecules but not that of solute. When a solution is separated from the solvent by it is known as semipermeable membrane.

Some example of it are as follows

- (a) Copper ferrocyanide  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ ;
- (b) Calcium phosphate membrane; and
- (c) Phenol saturated with water.

#### **(g) Reverse Osmosis :**

If a pressure greater than the osmotic pressure is applied on the concentrated solution, the solvent starts to flow from concentrated solution to dilute solution (or pure solvent). This is reverse osmosis. One of its chief uses is desalination of sea water to get pure drinking water.

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### *Illustration*



**Ans. (D)**

**Sol.** For ternary electrolyte, osmotic pressure =  $(0.05 \times 3)(R)(T)$

$$\text{Osmotic pressure of B} = 2P = (0.1)(R)(T) \text{ or } P = \frac{0.1}{2} RT$$

$$P = 0.05 RT$$

Since temperature is the same, comparing the two equa-

Since temperature is the same, comparing the two equations, we obtain  
the osmotic pressure of ternary electrolyte =  $3P$

2. The osmotic pressure of blood is 7.65 atm. at 310 K. An aqueous solution of glucose which is isotonic with blood has the percentage (wt./volume)

(A) 5.41      (B) 3.54      (C) 4.53      (D) 53.4

Ans. (A)

**Sol.** Since glucose and blood are isotonic, the osmotic pressures are the same. Therefore,

$$\pi_{\text{glucose}} = \pi_{\text{blood}}$$

$$\text{Or } 7.65 \times V = \frac{w}{180} \times 0.0821 \times 310 \quad [w = \text{amount of glucose present in } V \text{ litres of solution}]$$

$$\text{Or } 7.65 \times 180 = \frac{w}{V} \times 0.0821 \times 310$$

$$\text{Or } \frac{w}{V} = \frac{7.65 \times 180}{0.0821 \times 310} = 54.1 \text{ g L}^{-1} \text{ or } 5.41\%$$

### *Exercise*

1. A 250 mL water solution containing 48.0 g of sucrose,  $C_{12}H_{22}O_{11}$ , at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied above the solution in order to just prevent osmosis?

**Ans.** 13.8 atm

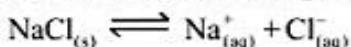
2. A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877%(w/v) of urea solution. Find molecular weight of urea.

**Ans.** 59.99

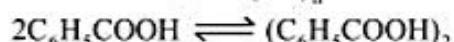
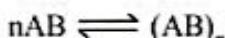
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## ABNORMAL MOLECULAR MASSES

Vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure are colligative properties which depend upon the fraction of solute and solvent particles in solution and not upon the chemical nature of the solute. If solute molecules dissociates in solution, there are more particles in solution and therefore, lowering of vapour pressure shows an increased effect.



If the solute molecules associates in solution, there are less particles in solution, and therefore lowering of vapour pressure shows a decreased effect.

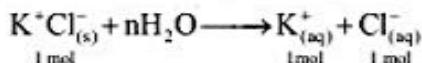


### The molecular mass of a solute is inversely proportional to its molality :

If colligative molality is 2 m, the calculated molecular mass is one-half of the actual molecular mass of the solute. If colligative molality is 3 m, the calculated molecular mass is one third of the actual molecular mass of the solute. The molecular mass of benzoic acid is 122 g/mol. But the molecular mass of benzoic acid dissolved in benzene is found to be 244 g/mol by using a colligative property. Benzoic acid associates to form a dimer and therefore its colligative molality is one-half of the molality of benzoic acid. As molecular mass of a solute is inversely proportional to molality, the molecular mass of benzoic acid determined using a colligative property is double the actual molecular mass of benzoic acid. We can summarize the results as:

#### (i) The extent of dissociation and colligative property :

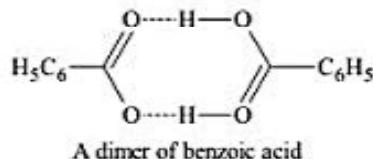
A solute dissociates completely or partially in solution makes available more particles than would otherwise be present in solution and therefore, a colligative property shows an increased effect. For example, molecular masses obtained of strong acids, bases and salts are much less than their normal values. As an example, one particle of potassium chloride on dissociation in water gives two particles,  $\text{K}^+$  and  $\text{Cl}^-$  and therefore, the molecular mass obtained by a colligative property is half of its normal molecular mass.



#### (ii) The extent of association and colligative property :

A solute that associates in solution provides less particles than would otherwise be present in solution and therefore, the colligative property shows the decreased effect. For example, benzoic acid in benzene is found to have molecular mass which is just twice its normal molecular mass.

It is found that compounds which are capable of forming hydrogen bonds, e.g., phenols, carboxylic acids, alcohols: because of association show decreased effect of colligative property.



## VANT HOFF FACTOR

In 1886, Van't Hoff, Jacobus Henricus (Dutch chemist, 1859,-1911) introduced a factor 'i' known as Van't Hoff factor to express the extent to association or dissociation of a solute in solution. It can be calculated as:

$$i = \frac{\text{number of solute particles actually present in solution}}{\text{number of solute particles dissolved}}$$

$$= \frac{\text{Observed colligative property}}{\text{normal colligative property}} = \frac{\text{observed molality}}{\text{normal molality}} = \frac{\text{normal molecular weight of solute}}{\text{observed molecular weight of solute}}$$

The Van't Hoff factor for a solute can be calculated by the following modified equations:

$$(i) \frac{P_A^0 - P_A}{P_A^0} = i X_B \quad (ii) \Delta T_f = i K_f m \quad (iii) \Delta T_b = i K_b m \quad (iv) \pi = i C RT$$

where C is molarity of the solution.

**Note:** For non-electrolytes;  $i = 1$

For electrolytes;  $i > 1$  (If solute particles undergo Dissociation in the solution)

$i < 1$  (If solute particles undergo Association in the solution)

### (iii) Application of Van't Hoff Factor :

#### (a) Calculation of Degree of Dissociation of solute particles:

No. of moles dissolved	$A_n$	$\rightleftharpoons$	$nA$
	1 mol		0
No. of moles after dissociation	$1 - \alpha$		$n\alpha$
Total number of moles present in solution = $(1 - \alpha) + n\alpha$			

$$\text{Van't Hoff factor, } i = \frac{\text{Moles of solute actually present in solution}}{\text{Moles of solute dissolved}}$$

$$= \frac{(1 - \alpha) + n\alpha}{1} = 1 + (n - 1)\alpha \quad \text{or} \quad \alpha = \frac{i - 1}{n - 1}$$

#### (b) Calculation of Degree of Association of solute particles:

Let  $n$  moles of the solute,  $A$ , associate to form  $(A)_n$ . If  $\alpha$  is the degree of association.

No. of moles dissolved	$nA$	$\rightleftharpoons$	$A_n$
	1 mol		0
No. of moles after dissociation	$1 - \alpha$		$\alpha/n$
Total number of moles present in solution = $(1 - \alpha) + \alpha/n$			

$$i = \left[ 1 - \alpha \left( 1 - \frac{1}{n} \right) \right] \quad \text{Hence} \quad \alpha = \frac{i - 1}{i - 1 - \frac{n}{n - 1}} = (i - 1) \times \frac{n}{1 - n}$$

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**Illustration**

1. Molal elevation constant  $K_b$  for water is 0.52 K/m. 0.1 molal solution of NaCl will boil at  
 (A) 100.52°C      (B) 100.052°C      (C) 101.04°C      (D) 100.104°C

**Ans.** (D)

**Sol.** If van't Hoff factor is  $i$ , then

$$\Delta T_b = i K_b \cdot m \text{ (for NaCl } i = 2\text{)} \\ = 2 \times 0.52 \cdot 0.1 = 0.104.$$

And, so the boiling point of solution will be 100.104°C.

2. A solution is prepared by dissolving 26.3g of CdSO<sub>4</sub> in 1000g water. The depression in freezing point of solution was found to be 0.284K. Calculate the Van't Hoff factor. The cryoscopic constant of water is 1.86K kg solvent mol<sup>-1</sup>- solute.

**Ans.** 1.21

**Sol.** Molecular mass CdSO<sub>4</sub> = 112.4 + 32 + 4 × 16 = 208.4 g/mol

$$\text{Molality CdSO}_4 = \frac{\text{Mass CdSO}_4}{\text{Molecular mass CdSO}_4 \times \text{Mass solvent in kg}}$$

$$= \frac{26.3\text{g}}{(208.4\text{g/mol}) \times \left(\frac{1000}{1000} \text{kg}\right)} = 0.216\text{m}$$

$$\Delta T_f = i K_f \cdot m \text{ or } i = \frac{\Delta T_f}{K_f \cdot m} = \frac{0.284\text{K}}{1.86\text{K/m} \times 0.216\text{m}} = 1.21$$

**Exercise**

1. A decimolar solution of potassium ferrocyanide is 50% dissociated at 300K. Calculate the osmotic pressure of the solution. ( $R=8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )

**Ans.**  $7.482 \times 10^5 \text{ Nm}^{-2}$

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

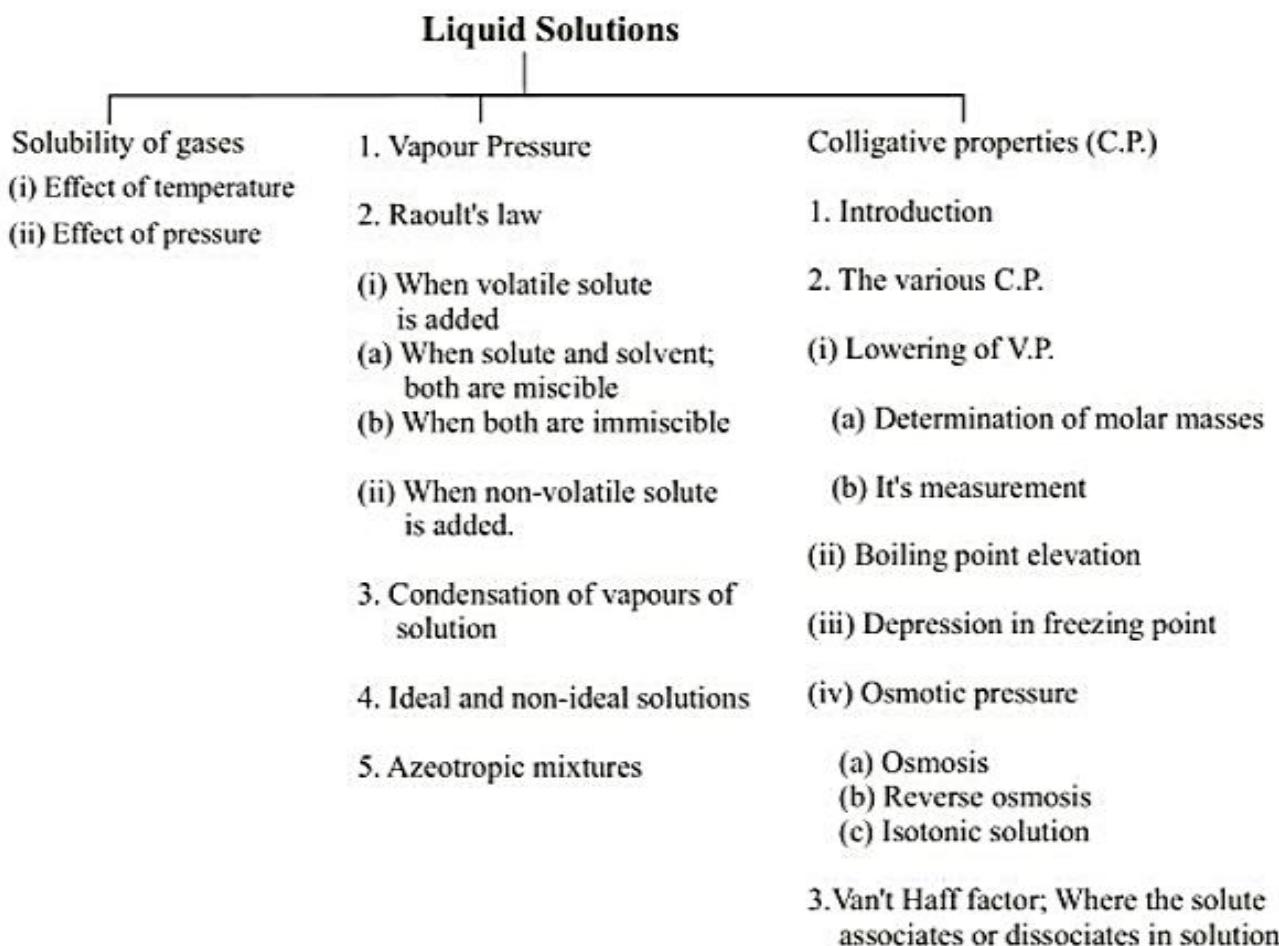
**Ans.** 0.95; 1.95

3. A 0.001 molal solution of a complex [MA<sub>8</sub>] in water has the freezing point of -0.0054°C. Assuming 100% ionization of the complex salt and  $K_f$  for H<sub>2</sub>O = 1.86 K.m<sup>-1</sup>, write the correct representation for the complex.

(A) [MA<sub>8</sub>]      (B) [MA<sub>7</sub>]A      (C\*) [MA<sub>6</sub>]A<sub>2</sub>      (D) [MA<sub>5</sub>]A<sub>3</sub>

**Ans.** (C)

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**THE ATLAS**

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## SOLVED EXAMPLES

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**OBJECTIVE**

**Q.1** 214.2 gram of sugar syrup contains 34.2 gram of sugar. Calculate (i) molality of the solution and (ii) mole fraction of the sugar in the syrup –

- (A) 0.555m, 0.0099    (B) 0.455m, 0.0110    (C) 0.355m, 0.0199    (D) None of these

**Ans.** (A)

**Sol.** (i) Mass of sugar = 34.2 gram. Number of moles of sugar =  $\frac{34.2}{\text{mol. mass}} = \frac{34.2}{34.2} = 0.1$

$$\text{Mass of water} = (214.2 - 34.2) = 180 \text{ gram or } \frac{180}{1000} \text{ kg}$$

$$\text{Number of moles of water} = \frac{180}{18} = 10$$

$$\text{Molality} = \frac{\text{No. of moles of sugar}}{\text{Mass of water in kg}} = \frac{0.1}{180} \times 1000 = 0.555 \text{ m}$$

(ii) Total no. of moles =  $10.0 + 0.1 = 10.1$

$$\text{Mole fraction of sugar} = \frac{\text{No. of moles of sugar}}{\text{Total number of moles}} = \frac{0.1}{10.1} = 0.0099$$

**Q.2** Calculate the amount of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) required to obtain 250 ml of semimolar solution.

- (A) 15.75 g    (B) 1.575 g    (C) 157.5 g    (D) None

**Ans.** (A)

**Sol.** Molarity of solution = 0.5 M

Volume of solution = 250 ml

$$\therefore \text{milli mole oxalic acid} = M \times V (\text{ml}) = \frac{1}{2} \times 250 \text{ or } \frac{w}{M} \times 1000 = 0.5 \times 250$$

$$\therefore w = \frac{250 \times 126}{2 \times 1000} = 15.76 \text{ g}$$

**Q.3** 15 gram of methyl alcohol is dissolved in 35 gram of water. What is the mass percentage of methyl alcohol in solution?

- (A) 30%    (B) 50%    (C) 70%    (D) 75%

**Ans.** (A)

**Sol.** Total mass of solution =  $(15 + 35)$  gram = 50 gram

$$\text{mass percentage of methyl alcohol} = \frac{\text{Mass of methyl alcohol}}{\text{Mass of solution}} \times 100 = \frac{15}{50} \times 100 = 30\%$$

**Q.4** 1.82 g metal required 32.5 mL of N HCl to dissolve it. What is equivalent weight for metal?

- (A) 65    (B) 75    (C) 56    (D) 90

**Ans.** (C)

---

Sol. ∴ Meq. of metal = Meq. of HCl or  $\frac{1.82}{E} \times 1000 = 32.5 \times 1$   
 $\therefore E = 56$

**Q.5** The vapour pressure of pure liquid 'A' at 310°C is 120 torr. The vapour pressure of this liquid in solution with liquid B is 72 torr. Calculate the mole fraction of 'A' in solution if the mixture obeys Raoult's law.

- (A) 0.06                      (B) 0.9                      (C) 0.3                      (D) 0.6

**Ans. (D)**

**Sol.** Given is vapour pressure of pure component 'A',  $P^{\circ}_A = 120$  torr

Partial pressure of A,  $P_A = 72$  torr

Suppose its mole fraction in solution is  $X_A$ , then according to Raoult's law.

$$P_A = P^{\circ}_A \cdot X_A$$

$$72 = 120 \times X_A \text{ or } X_A = \frac{72}{120} = 0.6$$

**Q.6** The degree of dissociation of  $\text{Ca}(\text{NO}_3)_2$  in dilute aqueous solution containing 7.0 g of salt per 100.0 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm Hg, the vapour pressure of the solution is

- (A) 748.3 mm Hg      (B) 1492.6 mm Hg      (C) 373.2 mm Hg      (D) 74.03 mm Hg

**Ans. (A)**

**Sol.** Moles of  $\text{Ca}(\text{NO}_3)_2 = \frac{7}{168}$  present in 100.0 g of water

Since dissociation is 70%, the total number of particles

$$= \frac{7}{168} \times 0.7 \times 3 = 0.0875 = n$$

$$\text{Also, moles of solvent} = \frac{100}{18} = 5.55 = N$$

Applying Raoult's law

$$\frac{P^{\circ} - P_{\text{solution}}}{P^{\circ}} = \frac{n}{n + N}$$

$$\text{Or } \frac{760 - p}{760} = \frac{0.087}{0.087 + 5.55}$$

$$\text{Or } 760 - p = 760 \left[ \frac{0.087}{5.637} \right] = 760[0.0154] = 11.704$$

$$\text{Or } p = 760 - 11.704 = 748.2 \text{ mm Hg}$$

- Q.7** The vapour pressure of a solvent is 20 torr whereas that of its dilute solution is 17 torr. The mole fraction of the solvent is

(A) 0.6    (B) 0.4    (C) 0.85    (D) 0.7

**Ans.** (C)

**Sol.** Vapour pressure of solvent  $p^\circ = 20$  torr and vapour pressure of solution  $p_s = 17$  torr.

$$\text{Therefore, } \frac{p^\circ - p_s}{p^\circ} = \text{mole fraction of solute}$$

$$\text{Or } \frac{20 - 17}{20} = 0.15 = \text{mole fraction of solute}$$

$$\text{Mole fraction of solvent} = 1 - 0.15 = 0.85$$

- Q.8** Methyl alcohol and ethyl alcohol have vapour pressure equal to 88.5 mm and 42.0 mm respectively at 45°C. If 16.0 g of methanol and 46.0 g of ethanol are mixed at 45°C, the mole fraction of methanol in the vapour is.....(the mixture may be taken as ideal solution).

(A) 0.467    (B) 0.502    (C) 0.513    (D) 0.556

**Ans.** (C)

**Sol.** For an ideal solution, obeying Raoult's law, the vapour pressure of mixture

$$p_{\text{mixture}} = \frac{P^\circ_{\text{methanol}} \cdot x^{\circ}_{\text{methanol}} + P^\circ_{\text{ethanol}} \cdot x^{\circ}_{\text{ethanol}}}{1}$$

$$\text{Or } p_{\text{mixture}} = 88.5 \times \frac{16/32}{\frac{16}{32} + \frac{46}{46}} + 42.0 \times \frac{46/46}{\frac{16}{32} + \frac{46}{46}}$$

$$p_{\text{mixture}} = 88.5 \times \frac{0.5}{1.5} + 42.0 \times \frac{1}{1.5} = 57.44 \text{ mm}$$

The mole fraction of any constituent 'i' in vapour phase is

$$= \frac{p_i}{p_{\text{total}}} \text{ that is } \frac{\text{vap. pressure of the constituent in solution}}{\text{Total vap. pressure of solution}}$$

$$= \frac{x_i p_i}{p_{\text{total}}} = 88.5 \times \left[ \frac{16/32}{16/32 + 46/46} \right] / 57.44$$

$$\text{Or the mole fraction of methanol in vapour phase} = 29.47 / 57.44 = 0.5130$$

- Q.9** The vapour pressure of benzene at 80°C is lowered by 10 mm when 2.0 g of a non-volatile substance is dissolved in 78 g of benzene. The vapour pressure of pure benzene at 80°C is 750 mm. The molar mass of the non-volatile substance is

(A) 150                      (B) 1050                      (C) 1500                      (D) 1550

**Ans.** (A)

**Sol.** If  $P^\circ$  is the vapour pressure of pure benzene and  $P$  the vapour pressure of solution,  $w$  the weight of non-volatile substance of molecular mass 'm' and  $w$  the weight of solvent benzene with molecular mass M,

$$\frac{P^\circ - P}{P^\circ} = \frac{w/M}{W/M} = \frac{wM}{WM}$$
 substituting the values

$$\frac{10}{750} = \frac{2 \times 78}{78 \times m}$$

$$0.0133 = \frac{156}{78 \times m}$$

$$\text{Or } m = \frac{156}{78 \times 0.0133} = 150.37 \sim 150$$

- Q.10** Calculate the molal elevation constant of water evaporates at 100°C with the absorption of 536 calories per gm     ( $R = 2$  cals)

(A) 0.519°C                      (B) 0.0519°C                      (C) 1.519°C                      (D) 2.519°C

**Ans.** (A)

**Sol.** Molal elevation constant of the solvent.

$$K_b = \frac{RT_b^2}{I_v \times 1000} = \frac{2 \times 373 \times 373}{536 \times 1000} = 0.519^\circ\text{C}$$

- Q.11** 0.15g of a substance dissolved in 15g of solvent boiled at a temperature higher by 0.216°C than that of the pure solvent. Calculate the molecular weight of the substance. Molal elevation constant for the solvent is 2.16°C.

(A) 216                              (B) 100                              (C) 178                              (D) None of these

**Ans.** (B)

**Sol.** Here it is given that

$$w = 0.15 \text{ g}, \quad \Delta T_b = 0.216^\circ\text{C}$$

$$W = 15 \text{ g} \quad K_b = 2.16^\circ\text{C} \quad m?$$

$$\text{Substituting values in the expression, } m = \frac{1000 \times K_b \times w}{\Delta T_b \times W} \quad m = \frac{1000 \times 2.16 \times 0.15}{0.216 \times 15} = 100$$

- Q.12** If latent heat of fusion of ice is 80 cals per g at 0°C, calculate molal depression constant for water.

(A) 18.63                              (B) 186.3                              (C) 1.863                              (D) 0.1863

**Ans.** (C)

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Sol.  $K_f = \frac{RT_f^2}{1000l_f}$  Here R = 2 cals,  $T_f = 0 + 273 = 273$  K,  $l_f = 80$  cals

$$K_f = \frac{2 \times 273 \times 273}{1000 \times 80} = 1.863$$

- Q.13** Osmotic pressure of a sugar solution at 24°C is 2.5 atmospheres. Determine the concentration of the solution in gm mole per litre.  
 (A) 0.0821 moles/litre (B) 1.082 moles/litre (C) 0.1025 moles/litre (D) 0.0827 moles/litre

**Ans.** (C)

**Sol.** Here it is given that

$$\pi = 2.5 \text{ atm}, T = 24 + 273 = 297^\circ\text{A}, S = 0.0821 \text{ lit. atm. deg}^{-1} \text{ mol}^{-1}, C = ?$$

$$\text{We know that } \pi = CST \quad \text{or} \quad C = \frac{\pi}{ST} = \frac{2.5}{0.0821 \times 297} = 0.1025 \text{ moles/litre}$$

- Q.14** Twenty grams of a substance were dissolved in 500 ml. of water and the osmotic pressure of the solution was found to be 600 mm of mercury at 15°C. Determine the molecular weight of the substance.  
 (A) 1120 (B) 1198 (C) 1200 (D) None of these

**Ans.** (B)

**Sol.** Here it is given that

$$w = 20 \text{ gm}; V = 500 \text{ ml.} = \frac{500}{1000} = 0.5 \text{ litre}$$

$$\pi = 600 \text{ mm} = \frac{600}{760} \text{ atm}; T = 15 + 273 = 288^\circ\text{A} \quad m = ?$$

According to Van't Hoff equation,

$$\pi V = nST \quad \pi V = \frac{w}{m} ST$$

$$\therefore m = \frac{wST}{\pi V} = \frac{20 \times 0.0821 \times 288 \times 760}{600 \times 0.5} = 1198$$

- Q.15** What weight of NaCl is added to one litre of water so that  $\Delta T_f/K_f = \frac{1}{500}$ ?

$$(A) 5.85 \text{ g} \quad (B) 0.585 \text{ g} \quad (C) 0.0585 \text{ g} \quad (D) 0.0855 \text{ g}$$

**Ans.** (C)

**Sol.** For NaCl  $i = 2$

$$\text{Or} \quad \Delta T_f = i \cdot K_f \cdot m$$

$$\Delta T_f/K_f = 2 \cdot m$$

$$\text{Or} \quad \frac{1}{500} = 2 \times m$$

Or molality =  $\frac{1}{1000}$  or  $\frac{1}{1000}$  moles are dissolved  $\text{Kg}^{-1}$  of water or approximately  $\frac{1}{1000}$  moles are present in 1.0 litre of water (considering molarity and molality to be the same)

$$\therefore \text{Weight of NaCl} = \frac{1}{1000} \times 58.5 \text{ g of NaCl}$$

$$= 0.0585 \text{ g of NaCl.}$$

### SUBJECTIVE

**Q.16** The addition of 3 gm of substance to 100 gm  $\text{CCl}_4$  ( $M = 154 \text{ gm mol}^{-1}$ ) raises the boiling point of  $\text{CCl}_4$  by  $0.60^\circ\text{C}$ .  $K_b$  of  $\text{CCl}_4$  is  $5.03 \text{ kg mol}^{-1} \text{ K}$ . Calculate

- (a) the freezing point depression
- (b) the relative lowering of vapour pressure
- (c) the osmotic pressure at  $298 \text{ K}$
- (d) the molar mass of the substance

Given  $K_f(\text{CCl}_4) = 31.8 \text{ kg mol}^{-1} \text{ K}$  and  $\rho$  (density) of solution =  $1.64 \text{ gm/cm}^3$

**Ans.** (a)  $3.79^\circ\text{C}$ , (b) 0.018, (c) 4.65 atm, (d) 251.5

**Sol.** (a)  $0.60 = K_b \times m$

$$\Delta T_f = K_f \times m$$

$$\frac{\Delta T_f}{0.60} = \frac{K_f}{K_b} \Rightarrow \frac{31.8}{5.03}$$

$$\Delta T_f = 3.79^\circ\text{C Ans.}$$

$$(b) m = \frac{\Delta T_b}{K_b} = \frac{0.60}{5.03} = 0.12$$

$$n_{\text{solute}} = 0.12, n_{\text{solvent}} = \frac{1000}{154} = 6.49$$

$$\text{Relative lowering of V.P.} = \frac{n_{\text{solute}}}{n_{\text{solvent}}} = \frac{0.12}{6.49} = 0.018 \text{ Ans.}$$

- (c) Amount of solute in 100 gm of solvent = 3 gm  
Amount of solute in 1000 gm of solvent = 30 gm

$$W_{\text{solution}} = 1030 \text{ gm}, V_{\text{solution}} = \frac{1030}{\rho_{\text{solution}}} = \frac{1030}{1.64} \text{ cm}^3 = \frac{1030}{1640} \text{ litre}$$

$$\pi = \frac{n_{\text{solute}} RT}{V_{\text{solution}}}$$

$$= \frac{0.12 \times 0.082 \times 298}{1030} = 4.65 \text{ (atm) Ans.}$$

$$(d) \quad 0.12 = \frac{30}{m_{\text{solute}}}$$

$$m_{\text{solute}} = \frac{3000}{0.12} = 250 \text{ (app) Ans.}$$

- Q.17** Vapour pressure of  $C_6H_6$  and  $C_7H_8$  mixture at  $50^\circ C$  is given by  $P \text{ (mm Hg)} = 180 X_B + 90$ , where  $X_B$  is the mole fraction of  $C_6H_6$ . A solution is prepared by mixing 936 g benzene and 736 g toluene and if the vapours over this solution are removed and condensed into liquid and again brought to the temperature of  $50^\circ C$ , what would be the new mole fraction of  $C_6H_6$  in the vapour state?

**Ans.** 0.93

**Sol.**  $C_6H_6 - B, \quad C_7H_8 - T$

$$n_B = \frac{936}{78}, \quad n_T = \frac{736}{92} = 8$$

$$X_B = \frac{n_B}{n_B + n_T} = \frac{12}{12 + 8} = 0.6$$

$$P = 180 X_B + 90$$

$$\text{Now } P = (P_B^0 - P_T^0) X_B + P_T^0$$

$$P_A^0 = 90 \text{ mm}, \quad P_T^0 = 270 \text{ mm}$$

$$P_T = 0.6 \times 270, \quad P = 180 \times 0.6 + 90$$

$$= 162 \text{ mm} \quad = 198 \text{ mm}$$

$$Y_B = \frac{P_B}{P} = \frac{162}{198} = \frac{9}{11}$$

Mole fraction of benzene in vapour

Now on condensation

$$X_B = Y_B \quad X_B = \frac{9}{11}$$

$$P_B = \frac{9}{11} \times 270 \text{ mm}, \quad P = 180 \times \frac{9}{11} + 90 = 90 \left( \frac{29}{11} \right) \text{ mm}$$

$$X_B = \frac{P_B}{P} = \frac{\frac{9}{11} \times 270}{90 \times \frac{29}{11}} = \frac{27}{29} = 0.93 \text{ Ans.}$$

- Q.18** The vapour pressure of two pure liquids, A and B that form an ideal solution are 300 and 800 torr respectively, at temperature T. A mixture of the vapour of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T. Calculate
- the composition of the first drop of the condensate,
  - the total pressure when this drop is formed,
  - the composition of the solution whose normal boiling point is T,
  - the pressure when only the last bubble of vapour remains, and
  - the composition of the last bubble.

**Ans.** (a) 0.47, (b) 565 torr, (c)  $x_A = 0.08$ ,  $x_B = 0.92$ , (d) 675 torr, (e)  $x'_A = 0.11$ ,  $x'_B = 0.89$

**Sol.** (a)  $P_A = X_A \times P_A^0$

$$P_T = X_A (P_A^0 - P_B^0) + P_B^0$$

$$564.7 = X_A (300 - 800) + 800$$

$$X_A = 0.47 \text{ Ans.}$$

$$(b) \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0} = \frac{1}{P_T}$$

$$\frac{0.25}{300} + \frac{0.75}{800} = \frac{1}{P_T}$$

$$P_T = 564.7 \text{ torr}$$

(c) At boiling temp vapour pressure = 760 torr

$$300 X_A + 800 X_B = 760$$

$$X_A (300 - 800) + 800 = 760$$

$$X_A = 0.08$$

$$X_B = 0.92$$

(d) When only the last bubble of vapour remains, we can assume that the composition of vapour is now the composition of the condensation

$$\therefore X_A = 0.25, \quad X_B = 0.75$$

$$P_i = X_A P_A^0 + X_B P_B^0$$

$$= 0.25 \times 300 + 0.75 \times 800$$

$$= 675 \text{ torr}$$

(e) Composition of last bubble =  $X_A$

$$X_A = Y_A$$

$$X_A = \frac{P_A}{P_T}$$

$$X_A = \frac{75}{675} = 0.11, \quad X_B = 1 - 0.11 = 0.89$$

**Q.19** When the mixture of two immiscible liquids (water and nitrobenzene) boils at 372 K and the vapour pressure at this temperature are 97.7 kPa ( $H_2O$ ) and 3.6 kPa ( $C_6H_5NO_2$ ). Calculate the weight % of nitrobenzene in the vapour.

**Ans.** 20.11 %

**Sol.** Let vapour contains  $W_1$  gm of  $C_6H_5NO_2$  and  $W_2$  gm of  $H_2O$

$$n_1 = \frac{w_1}{123}, \quad n_2 = \frac{w_2}{18}$$

for gases

Ratio of moles = Ratio of pressure

$$n_1 : n_2 = 3.6 : 97.7$$

$$\frac{w_1}{123} \times \frac{18}{w_2} = \frac{3.6}{97.7}$$

$$\frac{w_1}{w_2} = \frac{3.6 \times 123}{18 \times 97.7} = 0.252$$

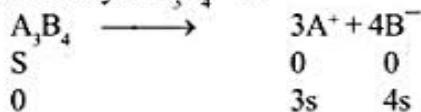
$$w_2 = w \text{ (let)}, w_1 = 0.252 w$$

$$\% w_1 = \frac{0.252w}{1.252w} \times 100 \\ = 20.11 \% \text{ Ans.}$$

- Q.20** A very dilute saturated solution of a sparingly soluble salt  $A_3B_4$  has a vapour pressure of 20 mm of Hg at temperature T, while pure water exerts a pressure of 20.0126 mm Hg at the same temperature. Calculate the solubility product constant of  $A_3B_4$  at the same temperature.

**Ans.**  $5.4 \times 10^{-13}$

**Sol.** Let the solubility of  $A_3B_4 = S$



$$\text{Solubility product of } A_3B_4 (K_{sp}) = (3S)^3 (4S)^4 = 6912 S^7$$

$$\text{For } A_3B_4, i = 7$$

To solve this problem we will assume

$$\text{Molarity} = \text{Molality and } w_{\text{solvent}} = w_{\text{solution}}$$

$$\text{Molality of } A_3B_4 = S$$

$$\Rightarrow n_{\text{solute}} = S, w_{\text{solvent}} = 1000 \text{ gm}$$

$$n_{\text{solvent}} = \frac{1000}{18} = 55.56$$

$$\frac{P_{\text{solvent}}^0 - P_{\text{solution}}}{P_{\text{solvent}}^0} = i \times \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$\frac{20.0126 - 20}{20.0126} = \frac{5 \times 7}{55.56}$$

$$S = 5 \times 10^{-3} \text{ M}$$

$$\therefore \text{Solubility product of } A_3B_4 (K_{sp}) = 6912 S^7 \\ = 6912 \times 5^7 \times 10^{-21} = 5.4 \times 10^{-13}$$

- Q.21** If the apparent degree of ionization of KCl in water at 290 K is 0.86. Calculate the mass of KCl which must be made up to 1 dm<sup>3</sup> of aqueous solution to the same osmotic pressure as the 4.0% solution of glucose at that temperature.

**Ans.** 8.9 gm

**Sol.** Glucose ( $C_6H_{12}O_6$ ),

$$\text{Molar concentration of glucose solution. (C}_1) = \frac{4.0 \times 1000}{180 \times 100} = \frac{2}{9} \text{ M}$$

$$\pi_1 = C_1 RT = \frac{2}{9} RT$$

For KCl solution.

$$n = 2, \alpha = 0.86,$$

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

$$i = 1.86$$

w = amount of KCl present in 1 dm<sup>3</sup> solution.

$\pi_2$  = Osmotic pressure of KCl solution

$$\pi_2 = 1.86 \times \frac{w RT}{74.5 \times 1}$$

$$\pi_1 = \pi_2$$

$$\frac{9}{2} RT = \frac{1.86 w RT}{74.5}$$

$$W = \frac{2 \times 74.50}{9 \times 1.86}$$

$$w = 8.9 \text{ gm}$$

∴ Mass of KCl present in 1 dm<sup>3</sup> of aq. solution = 8.9 gm

- Q.22** The specific conductivity of a 0.5 M aq. solution of monobasic acid HA at 27°C is 0.006 Scm<sup>-1</sup>. It's molar conductivity at infinite dilution is 200 S cm<sup>2</sup> mol<sup>-1</sup>. Calculate osmotic pressure (in atm) of 0.5 M HA (aq) solution at 27°C. Given R = 0.08 L-atm/K-mol

**Ans.** 12.72

$$\text{Sol. } \Lambda_m^c = \frac{K \times 1000}{C} = \frac{0.006 \times 1000}{0.500} = 12 \text{ S cm}^3 \text{ mol}^{-1}$$

$$\Lambda_m^o = 200 \text{ scm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^o} = 0.06$$

for HA, n = 2

$$\begin{aligned} i &= 1 + (n - 1) \alpha \\ &= 1 + (2 - 1) \times 0.6 \\ i &= 1.06 \end{aligned}$$

$$\begin{aligned} \pi &= i \times CRT \\ &= 1.06 \times 0.5 \times 0.082 \times 300 \\ \pi &= 12.72 \text{ atm} \end{aligned}$$

- Q.23** The freezing point of 0.02 mol fraction solution of acetic acid (A) in benzene (B) is 277.4K. Acetic acid exists partly as a dimer  $2A \rightleftharpoons A_2$ . Calculate equilibrium constant for the dimerisation. Freezing point of benzene is 278.4 K and its heat of fusion is 10.042 kJ mol<sup>-1</sup>.

**Ans.** K = 3.22

$$\text{Sol. } X_B = 0.02 \Rightarrow n_B = 0.02 \text{ and } n_A = 0.98$$

$$W_A = 0.98 \times 78 \text{ gm}$$

$$\text{Molality (m)} = \frac{n_B \times 1000}{W_A} = \frac{0.02 \times 1000}{0.98 \times 78} = 0.2616$$

$$\begin{aligned} K_f &= \frac{RT_f^2 m_A}{\Delta_f H \times 1000} = \frac{8.314 \times (278.4)^2 \times 78}{10042 \times 1000} \\ &= 5.00 \text{ K/m} \end{aligned}$$

$$\Delta T_f = i \times K_f m$$

$$1 = i \times 5 \times 0.2616$$

$$i = \frac{1}{5 \times 0.2616}$$

$$= 0.7645$$

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

As acetic acid dimerise, n = 2

$$i = 1 - \frac{\alpha}{2}$$

$$0.7645 = 1 - \frac{\alpha}{2}$$

$$\alpha = 0.4710$$

We assume : Molarity = Molality

$$\therefore \text{Molarity (C)} = 0.2616$$



$$\text{At } t = 0 \quad C \quad 0$$

$$\text{At equi.} \quad C(1-a) \quad \frac{Ca}{2}$$

$$K = \frac{[A_2]}{[A]^2} = \frac{Ca}{2C^2(1-a)^2} = \frac{a}{2C(1-a)^2} = \frac{0.471}{2 \times 0.2616 (0.529)^2} = 3.22$$

- Q.24** 1kg of an aqueous solution of Sucrose is cooled and maintained at  $-4^\circ\text{C}$ . How much ice will be separated out if the molality of the solution is 0.75?  $K_f(\text{H}_2\text{O}) = 1.86 \text{ Kg mol}^{-1}\text{K}$ .

**Sol.** Since molality of solution is .75 ,  
hence .75 moles of sucrose are present in 1000 g of solvent (i.e. water)

$$\because m_{\text{solution}} = m_{\text{water}} + m_{\text{sucrose}} = 1000 + .75 \times 342 = 1256.5 \text{ gm}$$

$$\therefore m_{\text{sucrose}} (\text{in kg}) = \frac{256.5}{1256.5} \times 1000 = 204.14 \text{ gm}, \quad m_{\text{water}} = 1000 - 204.14 = 795.86 \text{ gm}$$

$$\because \Delta T_f = K_f \times m \quad \Rightarrow 4 = 1.86 \times \frac{204.14 / 342}{W / 1000} \quad \Rightarrow W = 277.15$$

$$\therefore \text{amount of ice} = 795.86 - 277.15 = 518.31 \text{ gm}$$

- Q.25** River water is found to contain 11.7% NaCl, 9.5% MgCl<sub>2</sub>, and 8.4% NaHCO<sub>3</sub> by weight of solution. Calculate its normal boiling point assuming 90% ionization of NaCl, 70% ionization of MgCl<sub>2</sub> and 50% ionization of NaHCO<sub>3</sub> ( $K_b$  for water = 0.52)

Sol.  $n_{\text{NaCl}} = \frac{11.7}{58.5} = 0.2, \quad n_{\text{MgCl}_2} = \frac{9.5}{95} = 0.1, \quad n_{\text{NaHCO}_3} = \frac{8.4}{84} = 0.1$

 $i_{\text{NaCl}} = 1 + \alpha = 1 + 0.9 = 1.9, \quad i_{\text{MgCl}_2} = 1 + 2\alpha = 1 + 0.7 \times 2 = 2.4,$ 
 $i_{\text{NaHCO}_3} = 1 + 2\alpha = 1 + 0.5 \times 2 = 2.0$

Weight of solvent =  $100 - (11.7 + 9.5 + 8.4) = 70.4 \text{ g}$

$$\Delta T_b = \frac{(i_{\text{NaCl}} \times n_{\text{NaCl}} + i_{\text{MgCl}_2} \times n_{\text{MgCl}_2} + i_{\text{NaHCO}_3} \times n_{\text{NaHCO}_3}) \times K_b \times 1000}{\text{Weight of solvent}}$$

$$= \frac{(1.9 \times 0.2 + 2.4 \times 0.1 + 2 \times 0.1) \times 0.52 \times 1000}{70.4} = 5.94^\circ\text{C}$$

$\therefore$  Boiling point of solution =  $100 + 5.94 = 105.95^\circ\text{C}$

- Q.26** An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition C<sub>x</sub>H<sub>2x</sub>O<sub>x</sub> in 90 gm water boils at 101.24°C at 1.00 atmospheric pressure. What is the molecular formula?

$K_b(\text{H}_2\text{O}) = 0.512 \text{ K mol}^{-1} \text{ kg} \quad T_b(\text{H}_2\text{O}) = 100^\circ\text{C}$

Sol. Elevation in B.P. =  $101.24 - 100 = 1.24^\circ\text{C}$

$$\Delta T_b = K_b \times i \times \text{molality} \Rightarrow 1.24 = 0.512 \times \frac{288}{m} \times \frac{1000}{90} \quad (\therefore i = 1)$$

$\therefore m = 1321.2 \text{ gm mol}^{-1}$

molar mass of C<sub>x</sub>H<sub>2x</sub>O<sub>x</sub> =  $12x + 1 \times 2x + 16x = 30x$

$\therefore 30x = 1321.2$

$\therefore x = 44$

Hence the molecular formula is = C<sub>44</sub>H<sub>88</sub>O<sub>44</sub>

- Q.27** 30 ml of CH<sub>3</sub>OH (d = 0.7980 gm cm<sup>-3</sup>) and 70 ml of H<sub>2</sub>O (d = 0.9984 gm cm<sup>-3</sup>) are mixed at 25°C to form a solution of density 0.9575 gm cm<sup>-3</sup>. Calculate the freezing point of the solution. K<sub>f</sub>(H<sub>2</sub>O) is 1.86 Kg mol<sup>-1</sup> K. Also calculate its molarity

Sol. Weight of CH<sub>3</sub>OH (w<sub>1</sub>) =  $30 \text{ cm}^3 \times 0.7980 \text{ gm/cm}^3 = 23.94 \text{ gm}$

Weight of solvent (H<sub>2</sub>O) (w<sub>2</sub>) =  $70 \text{ cm}^3 \times 0.9984 \text{ gm cm}^3 = 69.888 \text{ gm}$

$$m = \frac{23.94}{32} \times \frac{1000}{69.88} = 10.7046 \text{ molal}$$

$\therefore \Delta T_f = K_f \times i \times \text{molality}, \quad (\text{for CH}_3\text{OH}, i = 1)$

$\Delta T_f = 1.86 \times 10.7046^\circ\text{C} = 19.91^\circ\text{C}$

Freezing point of the solution =  $0 - 19.91^\circ\text{C} = -19.91^\circ\text{C}$

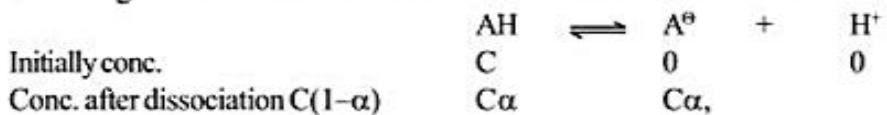
Weight of solution = weight of solute + weight of solvent =  $23.94 + 69.888 = 93.828 \text{ gm}$

$$\text{volume of the solution} = \frac{\text{wt. of the solution}}{\text{density of the solution}} = \frac{93.828}{0.95751} = 97.99 \text{ ml}$$

$$M(\text{molarity}) = \frac{23.94}{32} \times \frac{1000}{97.99} \text{ mol lit}^{-1} = 7.63 \text{ M}$$

- Q.28** Find  $K_a$ , the ionization constant of tartaric acid if a 0.100 molal aqueous solution of tartaric acid freezes at  $-0.205^\circ\text{C}$ . Assume that only the first ionization is of importance and that  $0.1 \text{ m} = 0.1 \text{ M}$ .  $K_f = 1.86 \text{ kg mol}^{-1} \text{ K}$ .

**Sol.** Assuming that the tartaric acid be a monobasic as AH. It ionizes as



$$\text{Here, } i = \frac{\text{C}(1-\alpha) + \text{C}\alpha + \text{C}\alpha}{\text{C}}, \text{ where } \alpha = \text{degree of dissociation} = \frac{\text{C}(1+\alpha)}{\text{C}} = 1+\alpha$$

Molal concentration = 0.1

$$\Delta T_f = K_f \times C_m \times i \Rightarrow 0.205 = 1.86 \times 0.1 \times (1+\alpha) \therefore \alpha = 0.1$$

$$K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{AH}]} = \frac{\text{C}\alpha \times \text{C}\alpha}{\text{C}(1-\alpha)} = \frac{\alpha^2 \text{C}}{1-\alpha} \quad K_a = \frac{(0.1)^2 \times 0.1}{1-0.1} = 1.11 \times 10^{-3}$$

$$\therefore K_a = 1.11 \times 10^{-3}$$

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