SOLUTION

1. **Definition of Solution :** When two or more chemically non-reacting substances are mixed and form homogeneous mixture is called solution.

When the solution is composed of only two chemical substances, it is termed a binary solution, similarly, it is called ternary and quaternary if it is composed of three and four components respectively.

Solution = solute + solvent

◆ **Solute :** Generally the component present in lesser amount than other component in solution is called solute.

◆ **Solvent :** Generally, the component present in greater amount than any or all other components is called the solvent.

* Physical state of solvent and solution is same.

Ex. In a syrup (liquid solution) containing 60% sugar (a solid) and 40% water (a liquid - same aggregation as solution), water is termed as the solvent.

2. **Dilute Solution :** A solution in which relatively a small amount of solute is dissolved in large amount of solvent is called a dilute solution.

3. **Concentrated solution :** A solution in which relatively a large amount of the solute is present is called a concentrated solution.

4. **Saturated solution :** The maximum amount of solute in grams, that can be dissolved in 100 g of a solvent at a particular temperature is called solubility of the solute and such a solution is called saturated solution.

5. **Super saturated solution :** A solution containing more amount of solute than that required for saturation of a given amount of solvent at a particular temperature, is called a supersaturated solution.

* It is unstable system.

6. **Types of Solution :**

	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.	Lquid	Gas	CO_2 gas dissolve in water (aerated drink), soda water.
5.	Lquid	Liquid	Mixture of miscible liquids e.g. alcohol in water.
6.	Lquid	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.

◆ **Sp. Note :** The solution of liquid in gas or solid in gas is not possible because the constituents can not form a homogeneous mixture.

7. **Properties of a solution :**

(i) A solution consists of a single phase i.e. it is a monophasic system.

(ii) A solution is uniform throughout, so it has uniform properties such as density refractive index, etc.

(iii) Size of solute particles in a solution is of the order $10^{-7} - 10^{-8}$ cm.

(iv) The components of a solution can not be easily separated by physical methods.

(v) The properties of a solution are the properties of its components. i.e. the components do not lose their properties when they form a solution.

(vi) The composition of a solution is not definite but can vary within certain limits.

(vii) Certain properties of solution such as density, viscosity, surface tension, boiling point, freezing point etc. vary with the composition of the solution.

8. **Percentage by weight :**

The number of grams of solute is dissolved in one gram of solution is called weight fraction of the solute. Thus,

$$\text{weight fraction} = \frac{w}{w+W}$$

Where 'w' grams of solute is dissolved in W grams of solvent.

$$\text{weight percent} = \frac{\text{weight of solute in grams} \times 100}{\text{weight of solution in grams.}}$$

$$w = \frac{w \times 100}{w+W}$$

9. **Percent by volume (Volume fraction) :**

This method is used for solutions of liquid in a liquid. The volume of liquid (solute) in mL dissolved in one mL of solution is called volume fraction.

$$\text{Volume fraction} = \frac{\text{Volume of liquid solute in mL}}{\text{volume of solution in mL}}$$

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

10. **Mole fraction** : The ratio of the number of moles of one component to the total number of all the components present in the solution, is called the mole fraction of that component.

Mole fraction of solute X_A is given by $$X_A = \frac{n_A}{n_A + n_B}$$

Mole fraction of solvent X_B is given by $$X_B = \frac{n_B}{n_A + n_B}$$

Where n_A is moles of solute of A & n_B is moles of solvent of B.

11. **Molarity (Molar concentration) :**

It is defined as the number of moles of the solute dissolved in per litre or per dm^3 of the solution, i.e.,

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

or Molarity Number of litres of solution = Number of moles of solute

Let w_A g of the solute of molecular mass m_A be dissolved in V litre of solution.

$$\text{Molarity of solution} = \frac{w_A}{m_A \times V}$$

or Molarity $m_A = \frac{w_A}{V}$ = Strength of the solution

If V is taken in mL (cm^3), then

$$\text{Molarity of the solution} = \frac{w_A}{m_A \times V} \times 1000$$

The unit of molarity is mol L^{-1} or mol dm^{-3}.

◆ **Molarity (second method) :**

Let d = density of solution in g/mL and let it contains x% solute by mass.

Then, mass of 1 litre solution = (1000 d)g

$$\text{Mass of solute in 1 litre} = \frac{x}{100} \times (1000 \times d)\text{g}$$

$$= (x \quad d \quad 10)\text{g}$$

Number of moles of solute in 1 litre

$$= \frac{\text{Mass of solute in gram}}{\text{Gram molecular mass of solute}} = \frac{x \times d \times 10}{m_A}$$

where m_A = molecular mass of solute

$$\therefore \quad M = \frac{x \times d \times 10}{m_A}$$

◆ **Molarity of dilute solution :**

Before dilution		After dilution
M_1V_1	=	M_2V_2

◆ **Molarity of mixing :**

Let there be three samples of solution (containing same solvent and solute) with their molarity M_1, M_2, M_3 and volumes V_1, V_2, V_3 respectively. These solutions are mixed; molarity of mixed solution may be given as :

$$M_1V_1 + M_2V_2 + M_3V_3 = M_R(V_1 + V_2 + V_3)$$

where, M_R = Resultant molarity

$V_1 + V_2 + V_3$ = Resultant volume after mixing

[Note : Molarity is dependent on volume, therefore, it depends on temperature.]

1M	Molar solution, i.e., molarity is 1
0.5 M or M/2	Semimolar
0.1 M or M/10	Decimolar
0.01 M or M/100	Centimolar
0.001 M or M/1000	Millimolar

12. Relation between molarity 'M' and mole fraction :

Let M be the molarity of solution, and x_A, x_B be mole fractions of solvent and solute, respectively.

Suppose n_A and n_B moles of solvent and solute are mixed to form solution.

Mass of solution = $n_Am_A + n_Bm_B$ ......(i)

where m_A and m_B are molar masses of solvent and solute, respectively.

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{(n_Am_A + n_Bm_B)}{d}$$

$$\text{Molarity} = \text{Number of moles of solute} \quad \frac{1000}{\text{Volume of solution}}$$

$$M = n_B \quad \frac{1000 \times d}{(n_Am_A + n_Bm_B)}$$

Dividing both numerator and denominator by $(n_A + n_B)$,

$$M = \left\{\frac{n_B}{n_A + n_B}\right\} \times \frac{1000 \times d}{\frac{n_A}{n_A + n_B} \times m_A + \frac{n_B}{n_A + n_B} \times m_B}$$

$$M = \frac{x_B \times 1000 \times d}{x_Am_A + x_Bm_B}$$

13. Normality (N) :

The number of equivalents or gram equivalents of solute dissolved in one litre of the solution is known as normality (N) of the solution.

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

$$= \frac{\text{weight of solute in gram}}{\text{equivalent weight } \times \text{volume of solution (litre)}}$$

$$= \frac{\text{strength of solution in gram / litre}}{\text{Equivalent weight of solute}}$$

Equivalent weight of a substance is that weight which reacts with or displaces one gram of hydrogen, 8 grams of oxygen or 35.5 grams of chlorine.

◆

Solutions are expressed as : 1N, $\frac{N}{2}, \frac{N}{10}, \frac{N}{100}, \frac{N}{1000}$, etc.

1N = Normal

= One gram equivalent of the solute per litre of solution

= Normality is 1

$\frac{N}{2}$ = Seminormal

= 0.5 g equivalent of the solute per litre of solution

= Normality is 0.5

$\frac{N}{10}$ = Decinormal

= 0.1g equivalent of the solute per litre of solution

= Normality is 0.1

$\frac{N}{100}$ = Centinormal

= 0.01g equivalent of the solute per litre of solution

= Normality is 0.01

$\frac{N}{1000}$ = Millinormal

= 0.001g equivalent of the solute per litre of solution

= Normality is 0.001

14. Molality (m) :

The number of moles or gram molecules of solute dissolve in 1000 gram of the solvent is called molality of the solution.

$$\text{Molality of a solution} = \frac{\text{Number of moles of solute}}{\text{Amount of solvent in kg.}}$$

$$= \frac{\text{Number of moles of solute} \times 1000}{\text{Amount of solvent in grams.}}$$

* It is independent of temperature.

15. **Formality** : It is the number of formula mass in grams present per litre of solution.

$$\text{formality} = \frac{\text{weight of solute in gram}}{\text{formula mass of solute in grams } \times \text{volume of solution in litre}}$$

◆ In case formula mass is equal to molecular mass, formality is equal to molarity.

◆ Depends on temperature.

16. **Concentration or strength of a solution (S) :**

The numbers of grams of solute dissolved in one litre solution is known as its strength in grams per litre.

* Strength in grams per litre

$$S = \frac{\text{wt. of solute in grams} \times 1000}{\text{volume of solution in mL}}$$

S = Molarity of solution × molecular wt. of solute.

S = Normality of solution × equivalent weight of solute.

17. **Parts per million (ppm)** : This method is used for expressing the concentration of very dilute solutions such as hardness of water, air pollution etc.

$$\text{ppm of substance} = \frac{\text{Mass of solute in gms} \times 10^6}{\text{Mass of solution}}$$

$$= \frac{\text{Volume of solute} \times 10^6}{\text{volume of solution}}$$

18. **Relation between molarity and normality :**

S = Molarity   molecular weight of solute

and   S = Normality   equivalent weight of solute

So we can write

Molarity   Molecular weight of solute = Normality   equivalent weight of solute.

$$\text{Normality} = \frac{\text{molarity} \times \text{molecular weight of solute}}{\text{equivalent weight of solute}}$$

$$= \frac{\text{molarity} \times \text{molecular weight of solute}}{\text{(molecular weight of solute/valency factor)}}$$

Normality =   molarity   valency factor

N = M   n   N ≥ M

19. **Relation between molality and molarity :**

$$\frac{\text{Molarity}}{\text{Molality}} = \frac{\text{Moles of solute}}{\text{volume of solution}} \times \frac{\text{mass of solvent}}{\text{moles of solute}}$$

$$= \frac{\text{mass of solvent(kg)}}{\text{volume of solution (in litre)}}$$

$$= \frac{\text{mass of solvent(in grams)}}{\text{volume of solution (in mL)}} = \frac{W}{V}$$

Let the density of the solution be d g. mL^{-1}

Mass of solution = V   d

Mass of solute = number of moles   molecular mass of solute

= n m_A

Mass of solvent(W) = mass of solution − Mass of solute

= (V   d) − (n m_A)

Thus $\dfrac{\text{Molarity}}{\text{Molality}} = \dfrac{(V \times d) - (n \times m_A)}{V}$

$$\text{Molality (m)} = \frac{\text{molarity} \times V}{(V \times d) - (n \times m_A)}$$

$$m = \frac{\text{molarity}}{d - \left(\frac{n}{V} \times m_A\right)}$$

$$m = \frac{\text{molarity}}{d - (\text{molarity} \times m_A)}$$

◆ **Sp. Note :**

If the density of solution is approximately 1. then

Molality > Molarity

◆ **Demal (D) :**

Demal (D) is another unit for expressing the concentration of a solution. It is equal to molar concentration at 0 C i.e., 1D respresents one mole of the solute present in one litre of the solution at 0 C.

Ex. If 0.4 gm of NaOH is present in 40 ml of solution. What is the molarity and normality [M.wt. of NaOH = 40]

Sol. We know that

$$\text{Molarity} = \frac{\text{wt. of solute} \times 1000}{\text{M.Wt. of solute} \times \text{volume of solution (mL)}} = \frac{0.4}{40 \times 40} \times 1000 = 0.25 \text{ M}$$

$$\text{and normality} = \frac{\text{wt.of solute}}{\text{Eq.wt. of solute} \times \text{volume of solution(mL)}} \times 1000$$

eq. wt. of NaOH = 40

so $N = \dfrac{0.4}{40 \times 40} \times 1000 = 0.25N$

◆ **Second method** N = m n

here n = 1, N = M, N = 0.25

Ex. The normality of 1.5M H_3PO_4 is –

Sol. Basicity of H_3PO_4 is 3

We know that N = M n

N = 1.5 3 = 4.5

Ex. How much volume of 10M HCl should be diluted with water to prepare 2.00 L of 5M HCl ?

Sol. In dilution the following equation is applicable :

M_1V_1 = M_2V_2

10M HCl = 5M HCl

10 V_1 = 5 2.00

$V_1 = \dfrac{5 \times 2.00}{10} = 1.00$ L

Ex. Find out the weight of H_2SO_4 in 150 mL, $\frac{N}{7}$ H_2SO_4.

Sol. $N = \frac{\text{Weight in gram}}{\text{equivalent weight} \times \text{volume}}$

wt. in gram = eq. wt N volume

$$= 49 \quad \frac{1}{7} \quad \frac{150}{1000} = \frac{21}{20} = 1.05 \text{ g}$$

Ex. Find out the molarity of 1 litre of 93% H_2SO_4 and its density is 1.84.

Sol. $\text{Molarity} = \frac{\text{Wt. in g} \times \text{density} \times 1000}{\text{molecular wt.} \times 100} = \frac{93 \times 1.84 \times 1000}{98 \times 100} = 78.68 \text{ M}$

Ex. A 100 cm^3 solution is prepared by dissolving 2g of NaOH in water. Calculate the normality of the solution.

Sol. 2 g NaOH = $\frac{2}{40}$ g. eq. = $\frac{1}{20}$ g eq.

$$N = \frac{\frac{1}{20}}{100} \times 1000 = \frac{1}{2}$$

Normality of solution = $\frac{N}{2}$

Ex. Find the percentage by weight and weight fraction of aspirin in the solution prepared by dissolving 3.65 g of aspirin in 25.08 g of water.

Sol. weight of solution = 3.65 + 25.08 = 28.73 g

weight fraction $= \frac{3.65}{28.73} = 0.127$

weight percent = 0.127 100 = 12.7%

Ex. A solution was prepared by adding 125 cm^3 of isopropyl alcohol to water until the volume of the solution was 175 cm^3. Find the volume fraction and volume percent of isopropyl alcohol in the solution.

Sol. volume of solute = 125 cm^3

volume of solution = 175 cm^3

$\therefore$ volume fraction $= \frac{125}{175} = 0.714$

and volume percent $= \frac{125}{175} \times 100 = 71.4\%$

Ex.3 The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/mL. Calculate the molarity and normality of the solution.

Sol. Volume of 100 g of the solution

$$= \frac{100}{d} = \frac{100}{1.09} \text{mL}$$

$$= \frac{100}{1.09 \times 1000} \text{ litre}$$

$$= \frac{1}{1.09 \times 10} \text{ litre}$$

Number of moles of H_2SO_4 in 100 g of the solution = $\frac{13}{98}$

$$\text{Molarity} = \frac{\text{No. of moles of } H_2SO_4}{\text{Volume of solution. in litre}} = \frac{13}{98} \times \frac{1.09 \times 10}{1} = 1.445 \text{ M}$$

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

$$\text{Molarity} = \frac{\%\text{ strength of solution} \times \text{density of solution} \times 10}{\text{Mol. mass}}$$

Similarly,

$$\text{Normality} = \frac{\%\text{ strength of solution} \times \text{density of solution} \times 10}{\text{Eq. mass}}$$

We know that,

Normality = Molarity n

$$= 1.445 \quad 2 \quad \left[n = \frac{\text{Mol. mass}}{\text{Eq. mass}} = \frac{98}{49} = 2 \right]$$

= 2.89 N

20. Vapour pressure :

At a constant temperature, the pressure exerted by the vapours of a liquid on its surface when they (liquid and its vapours) are in equilibrium, is know as vapour pressure.

◆ **Raoult's law :**

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

(i) For liquid – liquid solution :

Let a mixture (solution) be prepared by mixing n_A moles of liquid A and n_B moles of li quid B. Let P_A' and P_B' be the partial pressures of two constituents A and B in solution and P_A^0 and P_B^0 the vapour pressures in pure state respectivity.

Thus, according Raoult's law

$$P_A' = \frac{n_A}{n_A + n_B} PA^0 \qquad ....(1)$$

Partial pressure of A = mole fraction of A $P_A^0 = X_A P_A^0$

$$\text{and} \quad P_B' = \frac{n_B}{n_A + n_B} P_B^0 \qquad ....(2)$$

Partial pressure of B = mole fraction of B $P_B^0 = X_A P_B^0$

If total pressure be P_S, then

$$P_S = P_A' + P_B'$$

$$= \frac{n_A}{n_A + n_B} P_A^0 + \frac{n_B}{n_A + n_B} P_B^0$$

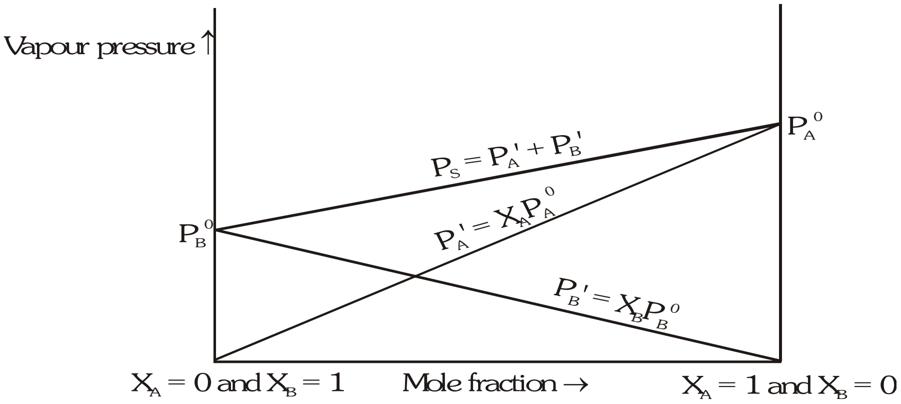
$$= X_A P_A^0 + X_B P_B^0 \qquad ....(3)$$

$$P_S = X_A P_A^0 + (1 - X_A) P_B^0 \qquad [\because X_A + X_B = 1]$$

$$P_S = X_A P_A^0 - X_A P_B^0 + P_B^0$$

$$P_S = X_A [P_A^0 - P_B^0] + P_B^0 \qquad .....(4)$$

Equation 1, 2 and 3 are the straight line equation so we can draw it as follows.



Ex. 1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mol. Octane (V.P. = 31 mm of Hg), form an ideal solution. Find out the vapour pressure of solution.

Sol. total mole = 1 + 4 = 5

Mole fraction of heptane = X_A = 1/5

Mole fraction of octane = X_B = 4/5

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

$$= \frac{1}{5} \times 92 + \frac{4}{5} \times 31$$

= 43.2 mm of Hg.

Ex. At 88 C benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88 C at 1 atm pressure, benzene – toluene form an ideal solution.

Sol. P_S = 760 torr, because solution boils at 88 C

Now 760 = 900 mole fraction of C_6H_6 + 360 [1 – mole fraction of C_6H_6]

$\therefore$ 760 = 900 a + 360 – 360 a

a = 0.74 where 'a' is mole fraction C_6H_6.

(ii) For Solid – liquid solution :

A = non volatile solids

B = volatile liquid

According to Raoult's law –

$\because \quad P_m = X_A P_A^0 + X_B P_B^0$

for A, $P_A^0 = 0$

$\therefore \quad P_m = X_B P_B^0$ ....(5)

Let $P_B^0 = P^0$ = Vapour pressure of pure state of solvent.

here X_B is mole fraction of solvent

$$P_S = \frac{n_B}{n_A + n_B} P^0 \qquad ....(6)$$

$$P_S \propto \frac{n_B}{n_A + n_B}$$

i.e. vapour pressure of solution ∝ mole fraction of solvent

$\Rightarrow P_S = X_B P_B^0$

$\Rightarrow P_S = (1 - X_A) P_B^0$

$\Rightarrow P_S = P_B^0 - X_A P_B^0$

$$\frac{P_B^0 - P_S}{P_B^0} = X_A$$

or $$\frac{P^0 - P_S}{P^0} = X_A \qquad ....(7)$$

or $$\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_A + n_B} \qquad ....(8)$$

or $$\frac{P^0}{P^0 - P_S} = \frac{n_A + n_B}{n_A}$$

or $$\frac{P^0}{P^0 - P_S} = 1 + \frac{n_B}{n_A}$$

or $$\frac{P^0}{P^0 - P_S} - 1 = \frac{n_B}{n_A}$$

or $$\frac{P_S}{P^0 - P_S} = \frac{n_B}{n_A}$$

$$\frac{P^0 - P_S}{P_S} = \frac{n_A}{n_B} \qquad ....(9)$$

or $$\frac{P^0 - P_S}{P_S} = \frac{w_A . m_B}{m_A . w_B}$$

or $$\frac{w\ M}{m\ W} \qquad ....(10)$$

Ex. The vapour pressure of benzene at 90 C is 1020 torr. A solution of 5 g of a solute in 58.5 g benzene has vapour pressure 990 torr. The molecular weight of the solute is?

Sol. $$\frac{P^0 - P_S}{P_S} = \frac{w \times M}{m \times W}$$

$$\frac{1020 - 990}{990} = \frac{5 \times 78}{m \times 58.5}$$

m = 220

21. Colligative properties :

Those physical properties of a solution which depend upon the number of particles in a given volume of the solution or the mole fraction of the solute are called colligative properties.

The following four properties are colligative properties :

(i) Lowering of vapour pressure of the solvent.

(ii) Elevation in boiling point of the solvent.

(iii) Depression in freezing point of solvent.

(iv) Osmotic pressure.

Colligative properties α No. of particles.
α No. of molecules (In the solution of non electrolyte)
α No. of ions (In the solution of electrolytes)
α No. of moles of solute
α Mole fraction of solute

◆ Equimetal solutions of different substances (non valatile, non electrolyte) have the same values of colligative properties.

◆ **Colligative properties are the properties of dilute solution :**

(i) Lowering of vapour pressure :

When a non-volatile solute is dissolved in a pure solvent, the vapour pressure of the solvent is lowered i.e. the vapour pressure of a solution is always lower than that of pure solvent, because the escaping tendency of solvent molecules decreases (due to lesser surface area of solution available for evaporation).

If at a certain temperature P is the vapour pressure of pure solvent, and P_s is the vapour pressure of solution then

Lowering of vapour pressure = $P - P_s$

Relative lowering of vapour pressure $= \dfrac{P^0 - P_s}{P^0}$

from equation (8)

$$\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_A + n_B}$$

for a more dilute solution $n_A <<< n_B$

so

$$\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B}$$

$$\frac{\Delta P}{P^0} = \frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B}$$

$$\frac{\Delta P}{P^0} = \frac{n_A}{n_B} \qquad \text{....(11)}$$

or relative lowering of vapour pressure

$$= \frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

◆ **Measurement of Relative Lowering in Vapour Pressure**

(Ostwald and Walker Method)

The apparatus used is shown in Fig. It consists of two sets of bulbs. The first set of three bulbs is filled with solution to half of their capcity and second set of another three bulbs is filled with the pure solvent.

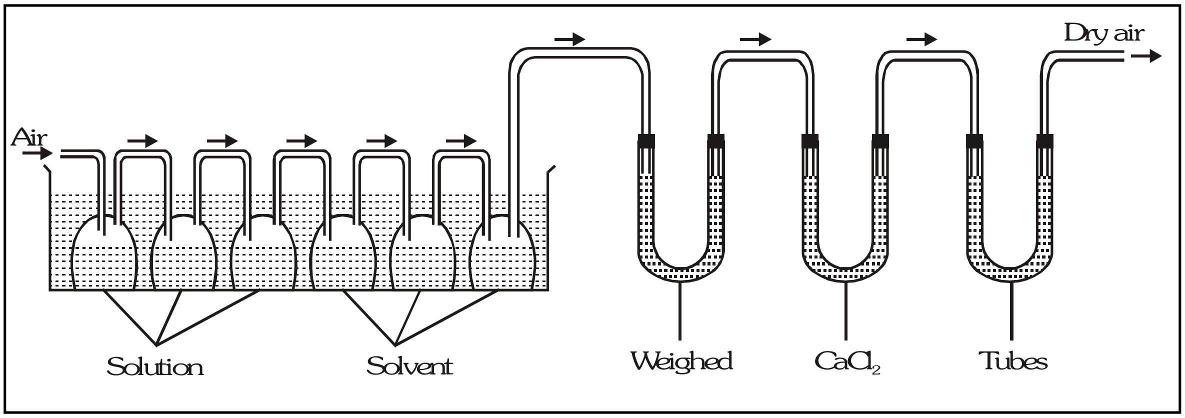


Fig. Ostwald and Walker method

Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents like P_2O_5, conc. H_2SO_4 etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

A current of pure dry air is bubbled through the series of bulbs as shown in fig. The air gets saturated with the vapour in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution, i.e., $p_0 - p_s$.

The two sets of bulbs are weighed again. The guard tubes are also weighed.

Loss in mass in the solution bulbs $\propto p_s$

Loss in mass in the solvent bulbs $\propto (p_0 - p_s)$

$$\text{Total loss in both sets of bulbs} \propto [p_s + (p_0 - p_s)]$$

$$\propto p_0$$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

$$\text{Thus, } \frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}}$$

$$= \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$$

Further, we know from Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{w_A / m_A}{w_A / m_A + w_B / m_B}$$

$$\therefore \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of gaurd tubes}} = \frac{w_A / m_A}{w_A / m_A + w_B / m_B}$$

The above relationship is used for calculation of molecular masses of non-volatile solutes.

For very dilute solutions, the following relationship can be applied :

$$\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of gaurd tubes}} = \frac{w_A m_B}{w_B m_A}$$

Ex. Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

Sol. According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n + N}$$

$$\text{or } \Delta p = \frac{n}{n + N} . p_0$$

Given : $n = \frac{50}{342} = 0.146$; $N = \frac{500}{18} = 27.78$ and $p_0 = 23.8$ mmHg

Substituting the values in the above equation,

$$\Delta p = \frac{0.146}{0.146 + 27.78} \times 23.8 = 0.124 \text{ mm Hg}$$

(ii) Elevation in boiling point (Ebullioscopy) :

The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure. i.e. 760 mm of Hg.

When a non-volatile solute is dissolved in a pure solvent, its vapour pressure is decreased. The difference ΔT_b of boiling points of the solution and pure solvent is called elevation in boiling point.

If T_0 is the boiling point of pure solvent and $(T_b)_s$ is the boiling point of the solution then,

$$(T_b)_s > T_0$$

and the elevation in boiling point

$$\Delta T_b = (T_b)_s - T_0$$

The elevation in boiling point (ΔT_b) is directly proportional to lowering of vapour pressure of the solution i.e.

$$\Delta T_b \propto P_o - P_s$$

or $\Delta T_b \propto \Delta P \propto \frac{n_A}{n_B}$

$$\therefore \quad \Delta T_b \propto \frac{n_A}{n_B} = \frac{w.M}{m.W}$$

for a solvent P^0 & M = const.

$$\therefore \quad \Delta T_b \propto \frac{w}{m.W}$$

$$\Delta T_b = \frac{Kw}{m.W}$$

where K = elevation constant

If $\frac{w}{m} = 1$ mole

and $w = 1$ g

then $\Delta T_b = K$

If $\frac{w}{m} = 1$ and $W = 100$ grams

$$\therefore \quad \Delta T_b = \frac{K}{100} = K' \quad = \text{ molecular elevation constant}$$

$$\therefore \quad K = 100\,K'$$

$$\Delta T_b = \frac{100K' \times w}{m \times W}$$

If $\frac{w}{m} = 1$ and $W = 1000$ gram

$$\therefore \quad \Delta T_b = \frac{K}{1000} = K_b \qquad \text{(molal elevation constant or Ebulloscopic constant)}$$

◆ K_b is defined as the elevation in boiling point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

$$\Delta T_b = \frac{K_b \times w \times 1000}{m \times W}$$

$$\Delta T_b = \frac{w}{m} \times \frac{1000}{W} \times K_b$$

$\therefore \quad \Delta T_b$ = molality K_b

$\therefore \quad \Delta T_b \propto$ molality

So we can say that elevation of boiling point = boiling point of the solution – boiling point of pure solvent

$$\Delta T_b = (T_b)_s - T_0$$

The elevation in boiling point of solution of non-electrolyte is proportional to its molality and equimolal solution of all the substances in the same solvent will show equal elevation in boiling points. These are known as Raoult's laws of elevation of boiling point.

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{RT_b^2}{1000\ L_v}$$

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 vaporisation of solvent in calories per gram.

For water

$$K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515$$

The molal elevation constant for some common solvents are given in the following table

Solvent	B.P. (C)	Molal elevation constant
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.67
Carbon tetra chloride	76.8	5.02
Benzene	80.0	2.70
Ethyl alcohol	78.4	1.15

Ex. 0.15 g of a substance dissolved in 15 g of solvent boiled at a temperature higher by 0.216 C than that of the pure solvent. What is the molecular weight of the substance. [K_b for solvent = 2.16 C]

Sol. Given K_b = 2.16 C

w = 0.15 g

ΔT_b = 0.216 C

W = 15 g

ΔT_b = molality K_b

$$\Delta T_b = \frac{w}{m \times W} \times 1000 \times K_b$$

$$0.216 = \frac{0.15}{m \times 15} \times 1000 \times 2.16$$

$$m = \frac{0.15 \times 1000 \times 2.16}{0.216 \times 15} = 100$$

Ex. The rise in boiling point of a solution containing 1.8 g glucose in 100 g of a solvent is 0.1 C. The molal elevation constant of the liquid is –

Sol. $\Delta\ T_b$ = molality K_b

$$\Delta T_b = \frac{w}{m \times W} \times 1000 \times K_b$$

$$K_b = \frac{\Delta T_b \times m \times W}{1000 \times w}$$

ΔT_b = 0.1 C

m = 180

W = 100

w = 1.8

$$K_b = \frac{180 \times 0.1 \times 100}{1000 \times 1.8} = 1.0$$

(iii) Depression in freezing point (Cryoscopy) :

The freezing point of a liquid is that temperature at which the liquid and its solid state exist in equilibrium with each other.

It may be defined as the temperature at which the liquid and solid states of a substance have the same vapour pressure.

When a non-volatile non-electrolyte is dissolved in a pure solvent the vapour pressure of the solvent is lowered

If T_o is the freezing point of pure solvent and $(T_f)_s$ is the freezing point of its solution then,

$$(T_f)_s < T_o$$

The difference in the freezing point of pure solvent and solution is the depression of freezing point (ΔT_f) Thus,

$$T_o - (T_f)_s = \Delta T_f$$

Depression in freezing point is directly proportional to the lowering of vapour pressure of solution.

$$\Delta T_f \propto P^0 - P_s$$

from Raoult's law for dilute solution :

$$\frac{P^0 - P_S}{P^0} = \frac{w_A}{m_A} \cdot \frac{m_B}{w_B}$$

or $$P^0 - P_S = \frac{w_A}{m_A} \cdot \frac{m_B}{w_B} \cdot P^0$$

for the pure solvent, P^0 and m_B are constant. therefore –

$$P^0 - P_S \propto \frac{w_A}{m_A w_B}$$

or $$\Delta P \propto \frac{w_A}{m_A w_B} \propto \Delta T$$

$$\Delta T_f = K \frac{w_A}{m_A w_B}$$

Where K is a constant, called depression constant .

when $\frac{w_A}{m_A} = 1$ (one mole of solute)

and $w_B = 1g.$

then $\Delta T_f = K$

If $\frac{w_A}{m_A} = 1$ and $w_B = 100$ g

then $\Delta T_f = \frac{K}{100} = K'$

K' is called molecular depression constant.

It is defined as the depression of freezing point produced when 1 mole of the solute is dissolved in 100 g of the solvent.

Thus K' = 100 K

So $$\Delta T_f = \frac{100K' \times w_A}{m_A \times w_B}$$

If $\frac{w_A}{m_A} = 1$ and $w_B = 1000$ g

$$\Delta T_f = \frac{K}{1000} = K_f$$

K_f is called molal depression constant.

◆ K_f is defined as the depression of freezing point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

or $\Delta T_f = \frac{1000K_f \times w_A}{m_A \times w_B}$ or $\Delta T_f =$ molality K_f

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

$$K_f = \frac{0.002\ T_f^2}{L_f}$$

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

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86$$

the molal depression constant for some common solvents are given in the following table

Solvent	F.P.(C)	Molal depression solvents
Water	0.0	1.86
Ethyl alcohol	– 114.6	1.99
Chloroform	– 63.5	4.70
Carbon tetra chloride	– 22.8	29.80
Benzene	5.5	5.12
Camphor	179.0	39.70

Ex. If freezing point of a solution prepared from 1.25 g of a non electrolyte and 20 g of water is 271.9 K, the molar mas of the solute will be –

Sol. Given = $(T_f)_s$ = 271.9 K

w = 1.25 g W = 20 g K_f = 1.86

$\Delta T_f = T_0 - (T_f)_s$

$= 273 - 271.9$

$\Delta T_f = 1.1$

$\Delta T_f =$ molality K_f

$$\Delta T_f = \frac{w}{m \times W} \times 1000 \times K_f$$

$$m = \frac{w \times 1000 \times K_f}{\Delta T_f \times W}$$

$$m = \frac{1.25 \times 1000 \times 1.86}{1.1 \times 20}$$

$m = 105.68$

Ex. Molal depression constant for water is 1.86 C. The freezing point of a 0.05 molal solution of a non electrolyte in water is :

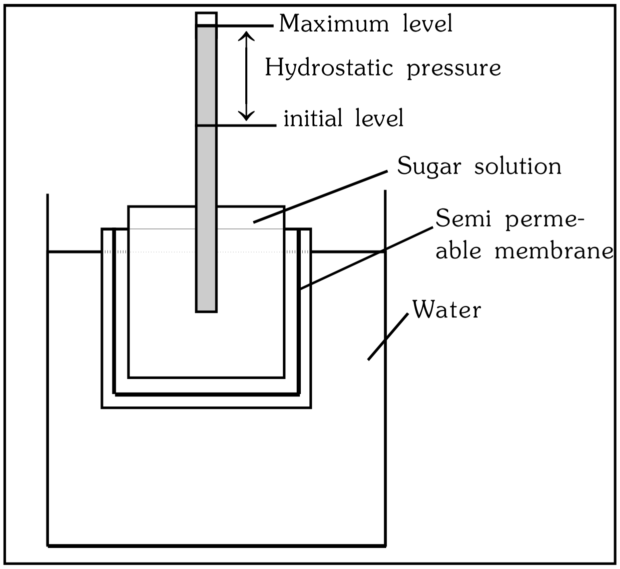
Sol. $\Delta T_f =$ molality K_f

$= 0.05 \quad 1.86 = 0.093$ C

$(T_f)_S = T_0 - 0.093 = 0 - 0.093$

$(T_f)_S = -0.093$

(iv) **Osmosis and osmotic pressure :**



◆ **Osmosis :**

Osmosis is defined as the spontaneous flow of solvent molecules through semipermeable membrane from a dilute solvent to a solution or from a dilute to a concentrated solution.

◆ **Osmotic presssure** (π) **:**

The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution.

or

The hydrostatic pressure built up on the solution which just stops the osmosis.

osmotic pressure = hydrostatic pressure

$$\pi = hdg$$

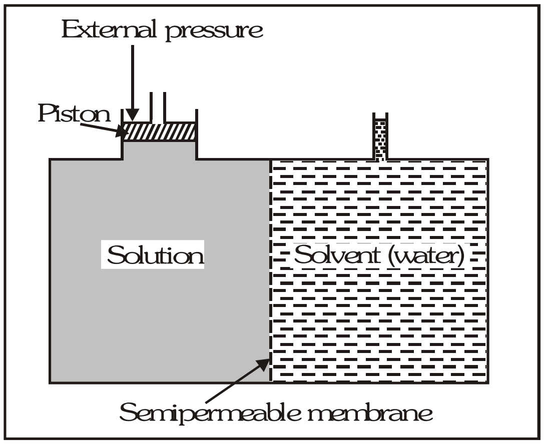
h = increase in level in the tube of unit cross section.

d = density of solution,

g = acceleration due to gravity

or

The external pressure which must be applied on the solution in order to stop the flow of the solvent into the solution through semipermeable membrane is equal to osmotic pressure.



22. **Van't Hoff law for dilute solution :**

The osmotic pressure (P or π) of a solution is directly proportional to its concentration(C) when the temperature is kept constant. The concentration of the solution containg in one gram mole in V litres is equal to 1/V.

thus $P \propto C$ (when temperature is constant)

or $P \propto \frac{1}{V}$

PV = constant or πV = constant

23. **Gay – Lussac – Van't Hoff law (Pressure - Temperature law) :**

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

$$P \propto T$$

or $\frac{P}{T} = \text{consant}$

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

Combining the two laws, i.e., when concentration and temperature both are changing, the osmotic pressure will be given by :

$P \propto CT$

or $P = kCT$

or $P = k.\frac{1}{V}.T \quad \left(\text{since, } C = \frac{1}{V}\right)$

or $PV = ST$ or $\pi V = ST$

S is called molar solution constant.

Here, V is the volume solution containing one gram mole of the solute. The value of S comes out to 0.082 litre atm K^{-1} mol^{-1} which is in agreement with the value of R, the molar gas constant. In case, the solution contains n gram moles in V litre, the general equation would become :

$PV = nST$

or $\pi V = nST$

Ex. A cane sugar solution has an osmotic pressure of 2.46 atm at 300 K. What is the strength of the solution.

Sol. $\pi V = nST$

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

or $C = \frac{\pi}{ST} = \frac{2.46}{300 \times 0.0821} = 0.1\ M$

◆ **Isotonic or iso-osmotic solution** :

Solutions which have the same osmotic pressure are termed isotonic or iso-osmotic solutions

$\pi_1 = \pi_2$

i.e. $C_1ST = C_2ST$

$C_1 = C_2$

◆ **Hypertonic solution**

A solution having higher osmotic pressure than some other solution is said to be called hypertonic solution.

◆ **Hypotonic solution**

A solution having a lower osmotic pressure relative to some other solution is called hypotonic solution.

◆ **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 $Cu_2[Fe(CN)_6]$;

(b) Calcium phosphate membrane; and

(c) Phenol saturated with water.

Ex. A solution containing 8.6 g urea in one litre was found to be isotonic with 0.5% (wt./vol.) solution of an organic, non-volatile solution. The molecular weight of latter is

Sol. Solutions are isotonic

so $\pi_1 = \pi_2$

$\frac{n_1}{V_1}ST = \frac{n_2}{V_2}ST \qquad \{\text{S \& T are constant}\}$

so, $\frac{n_1}{V_1} = \frac{n_2}{V_2}$

or $\left(\frac{w_1}{m_1 \times v_1}\right)_{urea} = \left(\frac{w_2}{m_2 \times v_2}\right)_{organic}$

or $\frac{8.6}{60 \times 1000} = \frac{0.5}{m_2 \times 100}$

$m_2 = 34.89$

◆

Reverse Osmosis :

If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis.

* Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.

24. Ideal Solutions :

A solution which obeys Rault's law exactly at all concentrations and at all temperatures is called an ideal solution.

An ideal solution possesses the following characteristics :

(i) Volume change of mixing shoule be zero.

$\Delta V_{mix} = 0$; $V_{solvent} + V_{solute} = V_{solution}$

(ii) Heat change on mixing should be zero.

$\Delta H_{mix} = 0$ (Heat is neither absorbed nor evolved)

(iii) There should be no chemical reaction between solvent and solute.

(iv) Solute molecules should not dissociate in the ideal solution.

(v) Solute molecules should not associate in ideal solution.

(vi) Ideal solution must obey Raoult's law at all concentrations.

Ex : (i) Benzene and toluene

(ii) Carbon tetrachloride and silicon tetra chloride.

(iii) n - Hexane and n - heptane

(iv) Ethylene dibromide and ethylene dichloride.

25. Non Ideal solutions :

Those solutions which do not obey Rault's law are called non-ideal solutions.

For such solutions $P_A \neq P_A^o \cdot X_A$

$P_B \neq P_B^o \cdot X_B$

Non ideal solutions are formed when the components differ much in their structures and polarities.

$\Delta H_{mixing} \neq$ zero

$\Delta V_{mixing} \neq$ zero

Non ideal solutions show either positive or negative deviations from Rault's law.

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

Sol. Let the vapour pressure of pure A be = p_A^0 ; and the vapour pressure of pure B be = p_B^0.

Total vapour pressure of solution (1 mole A + 3 mole B)

$= X_A.p_A^0 + X_B.p_B^0$ [X_A is mole fraction of A and X_B is mole fraction of B]

$$550 = \frac{1}{4}p_A^0 + \frac{3}{4}p_B^0 \quad \text{or} \quad 2200 = p_A^0 + 3p_B^0 \qquad ....(i)$$

Total vapour pressure of solution (1 mole A + 4 mole B) = $\frac{1}{5}p_A^0 + \frac{4}{5}p_B^0$

$$560 = \frac{1}{5}p_A^0 + \frac{4}{5}p_B^0$$

$$2800 = p_A^0 + p_B^0 \qquad ....(ii)$$

Solving eqs. (i) and (ii)

p_B^0 = 600 mm of Hg = vapour pressure of pure B

p_A^0 = 400 mm of Hg = vapour pressure of pure A

26. **Positive deviation from Rault's law :**

This deviation is shown when the forces of attraction between A – B molecules are less than forces of attraction between A – A and B – B molecules in the two liquids forming the solution.

$$P_A > P_A^\circ \cdot X_A$$

$$P_B > P_B^\circ \cdot X_B$$

The total vapour pressure of the solution will be greater than the corresponding vapour pressure expected in case of ideal, an ideal solution of same composition. i.e.

$$P_{total} > P_A^\circ \cdot X_A + P_B^\circ \cdot X_B$$

- $\Delta H_{mix} > 0$. Endothermic dissolution ; heat is absorbed.
- $\Delta V_{mix} > 0$. volume is increased after dissolution.
- 'A' and 'B' escape easily showing higher vapour pressure than the expected value.

Ex. (i) Ethanol and cyclohexane

(ii) Acetone and benzene

(iii) Water and methanol.

(iv) acetone + ethanol

(v) acetone + CS_2

(vi) water + ethanol

(vii) CCl_4 + toluene

(viii) CCl_4 + $CHCl_3$

27. **Negative deviation from Rault's law :**

In these solutions the A–B interaction are stronger than the A–A and B–B molecular interactions present in the two liquids forming the solution. For thus solutions showing –ve deviation.

$$P_A < P_A^\circ \cdot X_A$$

$$P_B < P_A^\circ \cdot X_B \quad \text{and} \quad P_{total} < P_A^\circ \cdot X_A + P_B^\circ \cdot X_B$$

- $\Delta H_{mix} < 0$; exothermic dissolution heat is evolved.
- $\Delta V_{mix} < 0$; volume is decreased during dissolution.

Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.

Ex. (i) Acetone and chloroform

(ii) Nitric acid and chloroform.

(iii) Water and HCl.

(iv) CH_3OH + CH_3COOH

(v) H_2O + HNO_3

(vi) Chloroform + diethyl ether

(vii) water + HCl

(viii) acetic acid + pyridine

(ix) chloroform + benezene

28. Relation between Dalton's Law and 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 fraction 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.

$p_A = Y_A P$ ....(i)

$p_B = Y_B P$ ....(ii)

$p_A = X_A P_A^0$ ....(iii)

$p_B = X_B P_B^0$ ....(iv)

Equating eqs. (i) and (iii),

$$Y_A P = X_A P_A^0$$

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

Similarly, equating eqs. (ii) and (iv),

$$Y_B = \frac{X_B P_B^0}{P} = \frac{p_B}{P}$$

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

29. Abnormal colligative properties :

It has been observed that difference in the observed and calculated molecular masses of solute is due to association or dissociation of solute molecules in solution. It results in a change in the number of particles in solution.

30. Association of solute particles :

The formation of a bigger molecule by the union of two, three or more solute molecules is called association.

Let 'n' simple molecules combine to give an associated molecule as :

$$n(X) \underset{\text{solvent}}{\overset{\text{non polar}}{\rightleftharpoons}} (X)_n$$

n single molecules	one bigger molecule.

As a result, the total number of particles in solution becomes less than the number of molecules initially dissolved in the solution and hence the colligative properties will have lower value.

As the molar mass of solute is inversely proportional to the colligative properties, so the molar mass of solute will be greater than theoretical value.

31. Dissociation of solute molecules :

Molecules of electrolytes undergo ionization or dissociation in ionizing solvents to give two or more particles in solution.

For example, AB ionizes in solution to give two particles.

$$AB \underset{\text{solvent}}{\overset{\text{ionizing}}{\rightleftharpoons}} A^+ + B^-$$

This dissociation results in an increase in the total number of particles, and therefore the value of colligative properties of such solutions will be higher.

As the colligative properties are inversely related to molecular weight, so the molecular weight of ionizable solute will be less than the theoretical value.

32. Van't Hoff factor (i) :

In order to express the extent of association or dissociation with certain solutes are expected to undergo in solution.

Van't Hoff in 1886, introduced a factor, called Van't Hoff factor (i). The factor i is defined as

$$i = \frac{\text{observed colligative property}}{\text{Normal colligative property}}$$

$$i = \frac{\text{Normal or actual molecular weight}}{\text{observed molecular mass.}}$$

In case of association of solute particles in solution, the observed molecular weight of solute being more than the normal, the value of factor 'i' is less than unity (i.e. $i < 1$), while for dissociation the value of i is greater than unity (i.e. $i > 1$), because the observed molecular weight has lesser value than normal molecular weight.

33. Van't Hoff factor and degree of dissociation :

The fraction of the total number of molecules which dissociates in the solution into simple ions or molecules is called the degree of dissociation.

$$i = \frac{\text{number of particles after dissociation}}{\text{Number of particles initially taken.}}$$

Calculation of 'i' :

Let, solute be A_xB_y

	A_xB_y	$\longrightarrow$	$x\,A^{y+}$ +	yB^{x-}
Initial mol	1		0	0
after dissociation	$1 - \alpha$		$x\alpha$	$y\alpha$

Total no. of solute particles

$= 1 - \alpha + x\alpha + y\alpha$

$= 1 - \alpha + \alpha\,(x + y)$

$= 1 - \alpha + n\alpha$ [where $x + y = n$ (total ions.)]

(i). observed colligative properties $\propto$ observed number of solute particles

observed colligative properties $\propto (1 - \alpha + n\alpha)$

(ii). Normal colligative properties $\propto 1$

$$\frac{\text{eq (i)}}{\text{eq (ii)}} \Rightarrow i = \frac{1-\alpha+n\alpha}{1}$$

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

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

for strong electrolytes : $\alpha = 1$ or 100% so $i = n$ (total no. of ions)

Ex. $NaCl \rightarrow Na^+ + Cl^-$ $(i = 2)$

Ex. $K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$ $(i = 3)$

Ex. for complex compound

$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$

$n = 5$

If $\alpha = 50\%$ then find Van't hoff factor 'i' = ?

Sol. $i = 1 - \alpha + n\alpha$

or $i = 1 - 0.5 + 5 \quad 0.5 = 3$

34. Van't Hoff factor and degree of association :

The fraction of the total number of molecules of the substance which is present as associated molecules is known as the degree of association.

$$i = \frac{\text{Number of particles after association}}{\text{Number of particles before association}}$$

Calculation of 'i' :

Let, solute be nA

	nA	$\longrightarrow$	$(A)_n$
Initial mol	1		0
after dissociation	$1 - \alpha$		α/n

Total no. of solute particles

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

(i). observed colligative properties $\propto$ observed number of solute particles.

observed colligative properties $\propto 1 - \alpha + \alpha/n$

(ii). Normal colligative properties $\propto 1$

$$\frac{\text{eq (i)}}{\text{eq (ii)}} \Rightarrow i = 1 - \alpha + \alpha/n$$

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

α = degree of assocation , n = no. of solute particles which are associated

Ex. A 5% solution of anhydrous $CaCl_2$ at 0 C developed 15 atm. Osmotic pressure. What is the degree of dissociation of $CaCl_2$.

Sol. 5 g. of $CaCl_2$ are present in 100 ml, so 111 g (mol. wt. of $CaCl_2$) will be present in

$$\frac{100 \times 111}{5 \times 1000} = 2.22 \text{ lit.}$$

Now $\pi V = ST$ $\{\because \; n = 1\}$

$$\text{or} \quad \pi = \frac{0.082 \times 273}{2.22} = \frac{22.47}{2.22} = 10.09 \text{ atm}$$

Van't Hoff factor

$$i = \frac{\text{Actual no. of particles in solution}}{\text{No. of particles taken}}$$

$$\text{and} \quad \alpha = \frac{i - 1}{n - 1}$$

here n = 3

$$\alpha = \frac{\frac{15}{10.09} - 1}{3 - 1} = \frac{4.91}{10.09 \times 2}$$

$\alpha = 0.2433$ or 24.33%

35. Distribution Law :

◆ **Nernst distribution law**

(a) A solute on addition between two immiscible solvents distributes itself in such a way that the ratio of its concentration in between two solvents remains constant at constant temperature provided the solute remains in same molecular state in both solvent.

(b) Let solute A be distributed in between two phases I and II, then according to the distribution law,

$$K = \frac{[A]\,\text{in phase I}}{[A]\,\text{in phase II}} = \frac{[C_A]_I}{[C_A]_{II}}$$

or $$K = \frac{\text{Moles of A in phase I}}{\text{Volume of phase I in litre}} \quad \frac{\text{Volume of phase II in litre}}{\text{Moles of A in phase II}}$$

or $$K = \frac{\text{wt. of A in phase I}}{\text{Volume of phase I in litre}} \quad \frac{\text{Volume of phase II in litre}}{\text{wt. of A in phase II}}$$

Where K is distribution coefficient or partition coefficient, a characteristic constant at the given temperature for given solute-solvent - I - solvent - II system.

(c) Also,

$$K \text{ in favor of I} = \frac{[C_A]_I}{[C_A]_{II}}$$

$$K \text{ in favor of II} = \frac{[C_A]_{II}}{[C_A]_I}$$

◆ **Condition for validity of law**

(a) Temperature should remain constant .

(b) Solution should be dilute.

(c) System must be heterogeneous, i.e., two solvents should be immiscible.

(d) Solute should not influence the immisicibility of two solvents.

(e) Solute neither dissociate nor associate in either of the solvent.

(f) Solute should be soluble in both solvents.

◆ **Solute showing dissociation in either of the solvent**

(a) Let AB be a solute which dissolves in solvent I during its distribution between two immiscible solvents I and II, then if C_1 is concentration of solute in phase I and C_2 its concentration of solute in phase II, according to distribution law.

$$K = \frac{C_1(1-\alpha)}{C_2}$$

Where α is the degree of dissociation of solute in solvent I.

◆ **Solute showing association either of the solvent**

(a) Let AB be a solute which associates in solvent II as

$$nAB \rightleftharpoons (AB)_n$$

during its distribution in between two solvents I and II.

(b) Then, if C_1 and C_2 are concentrations of solute in phase I and II respectively then according to distribution law,

$$K = \frac{C_1}{n\sqrt{C_2}}$$

Where n is association number and 100% association is assumed.

◆ **Extraction of solute in multistep operations**

(a) Let w g of a solute be present in V mL of solvent A. Now suppose V_1 mL of another solvent B are used to extract out solute from solvent A. Suppose n operations for extraction are made using V mL of solvent B, then

$$V_1 = n \quad v.$$

(b) Then the amount of solute (W_n) left unextracted in A after n operation using v mL of B in each step is given by

$$W_n = \left[\frac{KV}{v + KV}\right]^n W$$

It is clear from the equation of a solute from a given solution by extracting a liquid is more efficient when small volumes of extracting liquid are used in large number of operations.

Ex. 100 mL water and 50 mL ether mixture is shaken with succinic acid. At equilibrium ether layer contains 0.127 g and water layer contains 0.127 g and water layer contains 1.843 g of succinic acid. Calculate distribution coefficient in favour of water.

Sol. $$wK_{ether} = \frac{[\text{Succinic acid}]_{water}}{[\text{Succinic acid}]_{ether}}$$

$$wK_{ether} = \frac{1.843/100}{\frac{0.127}{50}} = \frac{1.843}{100} \quad \frac{50}{0.127} = 7.26$$

Ex. An organic substance has a normal molecular weight in water but gives a higher value in C_6H_6. The following data were obtained during a distribution experiment

Conc. of subs. in water ($g\,L^{-1}$)	0.01	0.02	0.24
Conc. of subs. in C_6H_6 ($g\,L^{-1}$)	1.848×10^{-5}	2.661×10^{-3}	1.089×10^{-2}

Find the degree of complexity of the substance in C_6H_6

Sol. Let, n be the complexity of acid in C_6H_6 and C_1, C_2 are concentrations of acid in water C_6H_6.

Then $$K = \frac{C_1}{n\sqrt{C_2}}$$

Taking log, $\log K = \log C_1 - \frac{1}{n} \log C_2$ ....(1)

using data in eq. .... (1)

$\log K = \log 0.01 - \frac{1}{n} \log 1.848 \quad 10^{-5}$ ....(2)

$\log K = \log 0.12 - \frac{1}{n} \log 2.661 \quad 10^{-3}$ ....(3)

$\log K = \log 0.24 - \frac{1}{n} \log 1.089 \quad 10^{-2}$ ....(4)

Solving equation (1) and (3) n = 1.999

Solving equation (3) and (4) n = 2.033

The value of n ≈ 2, which shows that organic substance form dimer in C_6H_6

36. Azeotropic mixtures :

Some liquids on mixing form azeotropes which are binary mixture having same composition in liquid and vapour phase and boil at a constant temperature. Azeotropic mixture cannot be separated by fractional distillation.

Types of Azeotropic mixtures

(i) Minimum boiling Azeotropic mixtures

The mixture of two liquids whose boiling point is less than either of the two pure components. They are formed by non-ideal solutions showing positive deviation. For example (95.5%) + water (4.5%) + water boils at 351.15 K.

(ii) Maximum boiling Azeotropic mixtures

The mixture of two liquids whose boiling point are more than either of the two pure components. They are formed by non-ideal solutions showing negative deviation. For example HNO_3 (68%) + water (32%) mixture boils at 393.5 K.

SOLVED EXAMPLE

Ex.1 A certain substance 'A' tetramerises in water to the extent of 80%. A solution of 2.5 g of A in 100 g of water lowers the freezing point by 0.3 C. The molar mass of A is :

(A) 122 (B) 31 (C) 244 (D) 62

Sol. **(D)**

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

$$0.8 = \frac{1-i}{1-\frac{1}{n}}; i = 0.4$$

$\Delta T = iK_f \quad m$

$$0.3 = 0.4 \quad 1.86 \quad \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = 0.4 \quad 1.86 \quad \frac{2.5 \times 1000}{m_B \times 100}$$

$m_B = 62$

Ex.2 Which of the following solutions will exhibit highest boiling point ?

(A) 0.01 M Na_2SO_4 (B) 0.01 M KNO_3 (C) 0.015 M urea (D) 0.015 M glucose

Sol. **(A)**

$\Delta T = i \quad K_b \quad m$

i m of Na_2SO_4 is highest, hence its boiling point will also be highest.

Na_2SO_4 i m = 3 0.01 = 0.03

KNO_3 i m = 2 0.01 = 0.02

Urea i m = 1 0.015 = 0.015

Glucose i m = 1 0.015 = 0.015

Ex.3 What is the osmotic pressure of 12% solution of can sugar (mol. wt. 342) at 17 C.

Sol. 12 g. sugar is dissolved in 100 mL thus 342 g. sugar is dissolved in

8 litres

Now, $\pi V = ST$ $\{\because n = 1\}$

$$\pi = \frac{ST}{V} = \frac{0.0821 \times 290}{2.85} = 8.35 \text{ atm}$$

Ex.4 Mixture of volatile components A and B has total vapour pressure (in torr) :

$P = 254 - 119\, x_A$

Where x_A is mol fraction of A in mixture.

Hence P_A and P_B are (in torr)

(A) 254, 119 (B) 119, 254 (C) 135, 254 (D) 154, 119

Sol. **(C)**

when $x_A = 0, x_B = 1$

$\therefore$ $P = P_B$

$\therefore$ $P_B = 254,$

when $x_A = 1, x_B = 0$

$\therefore$ $P_A = P = 254 - 119 = 135$

Ex.5 When mango is placed in dilute aqueous solution of hydrochloric acid, it ?

(A) Shrinks (B) Swells (C) Brusts (D) Nothing happens

Sol. **(A)**

The H^+ ion concentration in the medium is lower than that of H^+ concentration present in the mango juice, therefore osmotic pressure inside the mango is higher than that of aqueous hydrochloric acid. Therefore, H_2O will be passes out from the mango into aqueous hydrochloric acid. Therefore mango shrinks.

Ex.6 Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquids are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure, in bar, of a mixture of 25g of heptane and 35 g of octane ?

Sol. (A) Heptane C_7H_{16} $m_A = 100$

(B) Octane C_8H_{18} $m_B = 114$

$$n_A = \frac{w_A}{m_A} = \frac{25}{100} = 0.25 \; ; \quad n_B = \frac{35}{114} = 0.3$$

$$x_A = \frac{0.25}{0.25+0.30} = 0.45 \quad x_B = \frac{0.3}{0.25+0.30} = 0.55$$

$= 0.45$

$$p = p_A^0 x_A + p_B^0 x_B$$

$= 105.2 \quad 0.45 + 46.8 \quad 0.55$

$= 47.34 + 25.74 = 73.08$ kPa

Ex.7 The freezing point depression of 0.001 m $K_x[Fe(CN)_6]$ is $7.10 \quad 10^{-3}$ K. Determine the value of x. Given, $K_f = 1.86$ K kg mol^{-1} for water.

Sol. $\Delta x = i \quad K_f \quad m$

$7.10 \quad 10^{-3} = i \quad 1.86 \quad 0.001$

$i = 3.817$

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

$$1 = \frac{3.817-1}{(x+1)-1}$$

$x = 2.817 \approx 3$

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

Ex.8 The composition of vapour over a binary ideal solution is determined by the composition of the liquid. If x_A and y_A are the mole fractions of A in the liquid and vapour, respectively find the value of x_A for which $(y_A - x_A)$ has maximum. What is the value of the pressure at this composition ?

Sol. Since

$$y_A = \frac{x_A P_A^\circ}{P_B^\circ + (P_A^\circ - P_B^\circ)x_A}$$

Substracting x_A from both the sides, we get

$$y_A - x_A = \frac{x_A P_A^\circ}{P_B^\circ + (P_A^\circ - P_B^\circ)x_A} - x_A$$

Differentiating this with respect to x_A, we get

$$\frac{d(y_A - x_A)}{dx_A} = \frac{P_A^\circ}{P_A^\circ + (P_A^\circ - P_B^\circ)x_A} - \frac{x_A P_A^\circ \left(P_A^\circ - P_B^\circ\right)}{\left\{P_B^\circ + (P_A^\circ - P_B^\circ)x_A\right\}^2} - 1$$

The value of x_A at which $y_A - x_A$ has a maximum value can be obtained by setting the above differential equal to zero. Thus, we have

$$\frac{P_A^\circ}{P_A^\circ + (P_A^\circ - P_B^\circ)x_A} - \frac{x_A P_A^\circ \left(P_A^\circ - P_B^\circ\right)}{\left\{P_B^\circ + (P_A^\circ - P_B^\circ)x_A\right\}^2} - 1 = 0$$

Solving for x_A, we get $x_A = \dfrac{\sqrt{P_A^\circ P_B^\circ} - P_B^\circ}{P_A^\circ - P_B^\circ}$

The value of P at this composition is

$P = x_A\, P_A + x_B\, P_B$

or $P = P_B + (P_A - P_B)\, x_A$

or $P = P_B + (P_A - P_B)\left(\dfrac{\sqrt{P_A^\circ P_B^\circ} - P_B^\circ}{P_A^\circ - P_B^\circ}\right)$

or $P = \sqrt{P_A^\circ P_B^\circ}$

Ex.9 A dilute solution contains m mol of solute A in 1 kg of a solvent with molal elevation constant K_b. The solute dimerises in solution as $2A \rightleftharpoons A_2$. Show that equilibrium constant for the dimer formation is

$$K = \frac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$$

where ΔT_b is the elevation of the boiling point for the given solution. Assume molarity = molality

Sol. $2A \rightleftharpoons A_2$

m	0	initially
$(m - m\alpha)$	$\dfrac{m\alpha}{2}$	after dimerization
$m(1 - \alpha)$	$\dfrac{m\alpha}{2}$	

Where α is the degree of dimerization and m is molality which is also molarity (given). Hence due to dimerization, final molality = m

$$m(1 - \alpha) + \frac{m\alpha}{2} = m\left(1 - \frac{\alpha}{2}\right)$$

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

$$= 1 + \left(\frac{1}{2} - 1\right)\alpha$$

$$= \left(1 - \frac{\alpha}{2}\right)$$

$$\Delta T_b = K_b\ m\ \ i = K_b\ m\left(1 - \frac{\alpha}{2}\right)$$

$$\therefore \qquad \alpha = \frac{2(K_b m - \Delta T_b)}{K_b m}$$

equilibrium constant K for the dimer formation is

$$K = \frac{[A_2]}{[A]^2} = \frac{\frac{m\alpha}{2}}{m^2(1 - \alpha)^2} = \frac{\alpha}{2m(1 - \alpha)^2}$$

$$K = 2\left[\frac{K_b m - \Delta T_b}{K_b m}\right] \Big/ 2m\left[1 - \frac{2(K_b m - \Delta T_b)}{K_b m}\right]^2$$

$$K = \frac{K_b(K_b m - \Delta T_b)}{(K_b m - 2K_b m + 2\Delta T_b)^2}$$

$$K = \frac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$$ **Proved**

Ex.10 Distribution coefficient of an organic acid between water and benzene is 4.1 in favour of C_6H_6. If 5 g of acid is distributed in between 50 mL of benzene and 100 mL of water, calculate the concentration of acid in two solvents.

Sol. Let the amount of organic acid in

C_6H_6 layer = a g

volume of C_6H_6 = 50 mL

$\therefore$ concentration of acid in C_6H_6 = $\frac{a}{50}$ g mL^{-1}

since total amount of acid = 5 g

$\therefore$ Amount of acid in H_2O layer = (5 – a) g

and volume of H_2O = 100 mL

$\therefore$ Conc. of acid in H_2O $=\left(\frac{5-a}{100}\right)\frac{g}{mL}$

Now, $$K=\frac{\text{Conc. of acid in } C_6H_6}{\text{Conc. of acid in } H_2O}$$

$$=\frac{a}{50}\times\frac{100}{(5-a)}$$

$$\therefore \quad 4.1=\frac{a}{50}\times\frac{100}{(5-a)}$$

or a = 3.361 g.

$\therefore$ Amount of acid in 50 mL

C_6H_6 = 3.361 g

$\therefore$ acid concentration in C_6H_6 = $\frac{3.361}{50}\times1000 = 67.22$ g/L

Also, amount of acid in 100 mL H_2O = 5 – a = 5 – 3.361 = 1.639 g

$\therefore$ acid concentration in H_2O = $\frac{1.639}{100}\times1000 = 16.39$ g/L
