

UNIT-5

DILUTE SOLUTIONS

A solution is a homogeneous mixture of two or more substances having uniform properties throughout. When a lump of sugar or sodium chloride is added to water, it gets dispersed throughout water giving a homogeneous mixture.

The substances making up a solution are called components of the solution. If the solution contains only two components, the solution is called a binary solution. In a binary solution the component present in excess is called solvent and the component present in smaller amount is called solution. Sodium chloride solution contains two components, viz sodium chloride and water. Sodium chloride is the solution and water is the solvent in this solution.

Since there are three states of matter (gaseous, liquid and solid), there can be six possible different binary solutions depending on the physical state of the components: gas-gas, gas-liquid, liquid-liquid, liquid-solid, solid-gas and solid-solid.

When the amount of solute present in a solution is relatively small, the solution is said to be dilute. When the amount of solute present in a solution is relatively large, the solution is said to be concentrated. The above descriptions are qualitative. It is necessary to indicate the composition of any solution in terms of the amount of solute dissolved in definite amount of solvent or solution, generally called concentration.

Methods of expressing concentrations of solutions:

The concentration of any solution is expressed in any one of the following units:

(1) *Weight percent*: It is defined as the weight of solute in grams present in 100 grams of solution. A 10% solution of sugar contains 10 g of sugar in 100g of the solution.

(2) *Volume percent*: It is defined as the number of units of volume of solute present in 100 units of volume of solution. A 10% solution of ethyl alcohol contains 10 cm³ of alcohol in 100 cm³ of the solution.

(3) *Parts per million (ppm)*: The concentration of a solute in a solution in terms of parts per million is given by the equation,

$$\text{ppm} = \frac{\text{mass of the solute}}{\text{mass of the solution}} \times 10^6$$

This unit of concentration is generally used for the solutions when solute is present in very small quantity.

(4) **Molarity: (M)** It is defined as the number of moles of solute dissolved in 1 dm³ (litre) of solution at a given temperature. The molarity of solution is presented by M. It is expressed by the following equation:

$$M = \frac{n_2}{V}$$

Here, n_2 is the number of moles of solute and V is the volume of solution in dm³. The number of moles of the solute is calculated by dividing the mass in gram (w_2)

by its molar mass (M_2). Therefore, $M = \frac{W_2}{M_2 V}$. Molarity is expressed in

unit of mol per dm³ or mol dm⁻³. The symbol M used for molarities includes the above unit. A .02 M solution of glucose represents a solution of .02 mole of glucose present in 1 dm³ of solution.

(5) **Molality: (m)** It is defined as the number of moles of solute dissolved in 1 kg (1000 g) of solvent. The molality of the solution is represented by m.

$$m = \frac{n_2}{W_1}$$

where n_2 is the number of moles of solute and w_1 is the mass of the solvent in kilogram.

$$m = \frac{w_2}{M_1 \times w_1}$$

If w_1 is expressed in gram, then

$$m = \frac{1000 w_2}{w_1 M_1}$$

where w_2 is the mass of solute (in gram) and M_2 is the molar mass of solute. 1 molal solution of sodium chloride contains 58.5 g of sodium chloride per 1 kg of solvent.

(6) **Mole fraction: (x)** The mole fraction of a solute in a solution is the ratio between the number of moles of solute and solvent in the solution. The mole fraction of a solute in a solution can be expressed as

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

where x_2 is the mole fraction of solute, n_1 is the number of moles of solvent and n_2 is the number of moles of solute.

(7) **Normality: (N)** Normality of a solution is the number of gram equivalent mass of solute present in one dm³ of solution.

$$\text{Normality of a solution} = \frac{\text{Mass of solute/dm}^3}{\text{Equivalent mass of solute}}$$

Normality is represented by N. A 1 N solution of sodium hydroxide contains 40 g in 1 dm³ of solution. The equivalent mass of sodium hydroxide is 40. The use of normalities in expressing concentrations of solution is limited nowadays.

Problem: 1

Calculate the amount of glucose (C₆H₁₂O₆) needed to make up 1 dm³ of .2 M solution.

$$\text{Molarity } M = \frac{w_2}{M_2 V}$$

$$\text{Molarity } (M) = .2$$

$$\text{Mass of glucose } (w_2) = ?$$

$$\text{Molar mass of glucose } (M_2) = 180 \text{ g mol}^{-1}$$

$$\text{Volume of solution } (V) = 1 \text{ dm}^3$$

$$.2 = \frac{w_2}{180 \times 1}$$

$$w_2 = .2 \times 180 \times 1$$

$$= 36 \text{ g}$$

$$\text{Mass of glucose} = 36 \text{ g}$$

Problem: 2

What mass of glucose should be dissolved in 1 kg of water to get 0.1 molal solution?

$$\text{Molality} = \frac{w_2}{M_2 w_1}$$

$$\text{Molality } (m) = 0.1$$

$$\text{Mass of solute } (w_2) = ?$$

$$\text{Mass of solvent } (w_1) = 1 \text{ kg (1000 g)}$$

$$\text{Molar mass of solute } (M_2) = 180 \text{ g mol}^{-1}$$

$$0.1 = \frac{w_2}{1 \times 180}$$

$$w_2 = 1 \times 180 \times 0.1$$

$$= 18 \text{ g.}$$

If w_1 is expressed in gram, then

$$m = \frac{1000 \times w_2}{M_2 w_1}$$

$$0.1 = \frac{1000 \times w_2}{180 \times 1000}$$

$$w_2 = \frac{1000 \times 180 \times 0.1}{1000} = 18 \text{ g}$$

$$\text{Mass of glucose} = 18 \text{ g}$$

Problem: 3

A solution contains 5.85 g of sodium chloride and 90 g of water. What is the

mole fraction of sodium chloride?

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

$$= \frac{5.85}{58.5} = 0.1$$

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

$$= \frac{90}{18} = 5$$

$$\text{Molefraction, } x_2 = \frac{n_2}{n_1 + n_2}$$

$$\text{Mole fraction of sodium chloride } (x_2) = \frac{0.1}{5 + 0.1}$$

$$= \frac{0.1}{5.1} = 0.0196$$

$$x_2 = 0.0196.$$

Problem: 4

Calculate the mass of sodium hydroxide that must be used to prepare 500 cm³ of 0.1N solution?

$$\text{Mass of solute / dm}^3 = \text{Normality} \times \text{Equivalent mass of solute}$$

$$= 0.1 \times 40$$

$$= 4 \text{ g.}$$

$$\text{Mass of solute in 500 cm}^3 = 2 \text{ g.}$$

Vapour pressure of a liquid

When a liquid is placed in a closed vessel, some molecules at the surface of the liquid escape from the surface and constitute vapour above the liquid. This phenomenon is called evaporation. When the concentration of vapour increases, some vapour molecules pass back into the liquid. This process is called condensation. Finally a state is reached at which the rate of evaporation is equal to the rate of condensation. Now the system is said to be in dynamic or kinetic equilibrium. At this stage, the vapour reaches its maximum concentration and exerts maximum pressure. The pressure exerted by the vapour is known as the saturated vapour pressure.

The vapour pressure of a liquid at a given temperature is the pressure of the saturated vapour which exists over the liquid at the state of dynamic equilibrium with the liquid.

- (i) The saturated vapour pressure exerted by the vapour above the liquid is independent of the amount of the liquid present.
- (ii) The saturated vapour pressure of a liquid increases with temperature. As

the temperature increases more number of molecules escape to vapour state and increase the vapour pressure.

(iii) The vapour pressure at a given temperature depends upon the nature of the liquid. e.g. The vapour pressure of carbon tetrachloride is higher than that of water. The intermolecular bonding in water is stronger than that in carbon tetrachloride. Therefore, carbon tetrachloride evaporates faster than an equal volume of water at that temperature.

Colligative properties

There are certain properties which are common to all solutions containing non volatile solutes. These properties vary with the composition of the solution. The properties which depend on the total number of solute particles present in a fixed amount of solvent are called 'colligative properties'. The most important colligative properties of the solution are the vapour pressure, the boiling point, the freezing point and the osmotic pressure. The laws governing these colligative properties are generally known as the laws of dilute solutions.

Raoult's law

If a non volatile solute is added to a solvent to prepare a solution, the vapour pressure of the solution is found to be less than that of pure solvent. Raoult's law gives the relationship between the concentration of non volatile solute and the lowering of vapour pressure produced by it. The law can be stated as follows. The relative lowering of vapour pressure of a solution containing a non volatile solute is equal to the mole fraction of the solute in the solution.

If p_0 is the vapour pressure of pure solvent and p is the vapour pressure of the solution at the same temperature, the difference $p_0 - p$ is the lowering of vapour pressure. The ratio of the lowering of vapour pressure to the vapour pressure of the pure solvent is known as the relative lowering of vapour pressure.

$$\text{The relative lowering of vapour pressure} = \frac{p_0 - p}{p_0} \quad \dots (1)$$

$$\text{According to Raoult's law, } = \frac{p_0 - p}{p_0} = \frac{n_2}{n_1 + n_2} = x_2 \quad \dots (1)$$

Here, n_1 is the number of moles of the solvent and n_2 is the number of moles of the solute. The ratio, $\frac{n_2}{n_1 + n_2}$ is the mole fraction of the solute in the solution.

If the solution used is dilute, the number of moles of the solute (n_2) is small as compared with the number of moles of the solvent (n_1). Therefore n_2 is negligible ($n_1 + n_2 \cong n_1$) compared to the value of n_1 in the above equation (1). Therefore,

$$\frac{p_0 - p}{p_0} = \frac{n_2}{n_1} \quad \dots (2)$$

If w_1 is the mass of the solvent of molar mass M_1 and w_2 is the mass of the solute of molar mass M_2 , then

$$n_1 = w_1/M_1 \text{ and } n_2 = w_2/M_2$$

Substituting these values in the equation (2)

$$\frac{p_0 - p}{p_0} = \frac{w_2}{M_2} \times \frac{M_1}{w_1} \quad \dots (3)$$

The measurement of lowering of vapour pressure of solution enables the determination of the molar mass of the dissolved solute.

Ideal solutions

Ideal solutions are those which obey Raoult's law. The properties of an ideal solution are the average of the properties of its components in proportion to their mole fractions.

Determination of vapour pressure lowering and molar mass of a solute:

The relative lowering of vapour pressure can be measured by the method of Ostwald and Walker. The apparatus used is shown in Fig.5.1.

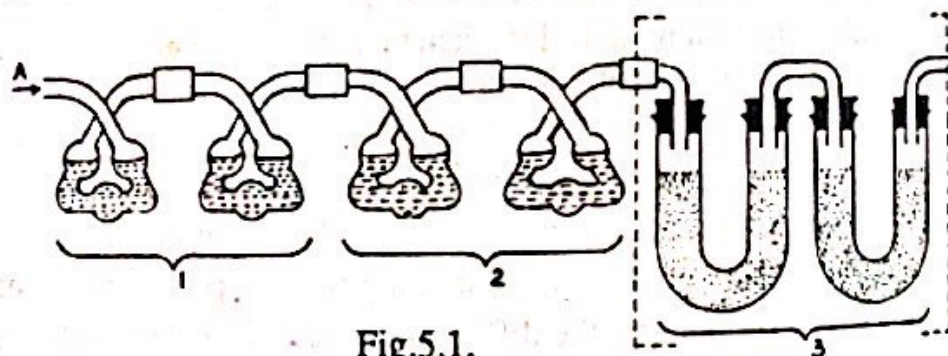


Fig.5.1.

Ostwald and Walker method of measuring relative lowering of vapour pressure.

A) Dry air 1) solution 2) solvent 3) Calcium Chloride Tubes

In this method a slow stream of dry air is passed through a weighed series of bulbs containing the solution. The air absorbs a mass of vapour proportional to the vapour pressure of the solution. Therefore, there is decrease in mass (m_1) of the first series of bulbs. This loss is proportional to the vapour pressure of the solution (p).

The air from the solvent bulbs is then passed through a similar series of bulbs of known mass, containing pure solvent. The air takes up more vapour as the vapour pressure of the solvent is greater than that of the solution. Therefore, there is loss in mass (m_2) of the second bulbs. This loss in mass is proportional to lowering of vapour pressure ($p_0 - p$).

In the case of aqueous solutions, the saturated air from solvent bulbs is then passed through weighed U-tubes containing anhydrous calcium chloride. There is an increase in mass of the U-tubes. This gain in mass is proportional to the vapour pressure of the pure solvent, p_0 .

The two sets of bulbs containing solution and solvent are accurately weighed before and after the passage of air. The loss of masses of the two sets of bulbs thus gives the relative lowering of vapour pressure.

$$\frac{p_0 - p}{p_0} = \frac{\text{decrease in mass of the solvent bulbs } (m_2)}{\text{decrease in the mass of the solution bulbs } (m_1) + \text{decrease in the mass of the solvent bulbs } (m_2)}$$

$$\frac{p_0 - p}{p_0} = \frac{m_2}{m_1 + m_2} = \frac{n_2}{n_1 + n_2} \quad n_1 \gg n_2$$

For dilute solution, $\frac{p_0 - p}{p_0} = \frac{m_2}{m_1 + m_2} = \frac{n_2}{n_1}$

$$\frac{p_0 - p}{p_0} = \frac{m_2}{m_1 + m_2} = \frac{w_2 / m_2}{w_1 / m_1} = \frac{w_2 M_1}{M_2 w_1}$$

$$M_2 = \frac{w_2 M_1 (m_1 + m_2)}{w_1 m_2} = \frac{w_2 m_1}{w_1} \left(\frac{p_0}{p_0 - p} \right)$$

Thus the molar mass of the solute can be calculated.

Problem: 5

The lowering of vapour pressure of a solution of 108.2 g of a substance in 1000 g of water at 20°C is 24.79 N m⁻². The vapour pressure of water at 20°C is 2.338 k N m⁻². Calculate the molar mass of the substance.

$$\frac{p_0 - p}{p_0} = \frac{w_2}{M_2} \times \frac{M_1}{w_1}$$

$$M_2 = \frac{w_2 \times M_1 \times p_0}{w_1 \times (p_0 - p)}$$

$$p_0 - p = 24.79 \text{ N m}^{-2}$$

$$p_0 = 2.338 \times 10^3 \text{ N m}^{-2}$$

$$w_1 = 1000 \text{ g}$$

$$w_2 = 108.2 \text{ g}$$

$$M_1 = 18 \text{ g mol}^{-1}$$

$$M_2 = ?$$

$$M_2 = \frac{108.2 \times 18 \times 2.338 \times 10^3}{1000 \times 24.79}$$

$$= 183.7 \text{ g mol}^{-1}$$

Problem: 6

A current of dry air is passed through a solution containing 4 g of phenol in 50 g of water, then through pure water. The loss in mass in the solution is 2.76 g; in the water the loss is 0.042 g. Calculate the molar mass of phenol.

$$\frac{\text{loss in mass of the solvent bulbs}}{\text{loss in mass of both the bulbs}} = \frac{\text{Mass of the solute / molar mass of the solute}}{\text{Mass of the solvent / molar mass of the solvent.}}$$

$$\frac{m_2}{m_1 + m_2} = \frac{w_2 M_1}{M_2 w_1}$$

$$\text{loss in mass of the solvent bulb } (m_2) = 0.042 \text{ g}$$

$$\text{loss in mass of the solution bulb } (m_1 + m_2) = 2.76 \text{ g}$$

$$\text{mass of the solute } (w_2) = 4 \text{ g}$$

$$\text{mass of the solvent } (w_1) = 50 \text{ g}$$

$$\text{molar mass of the solute } (M_2) = ?$$

$$\text{molar mass of water } (M_1) = 18 \text{ g mol}^{-1}$$

$$\frac{0.042}{0.042 + 2.76} = \frac{4 / M_2}{50 / 18}$$

$$\frac{0.042}{2.802} = \frac{4 \times 18}{50 \times M_2}$$

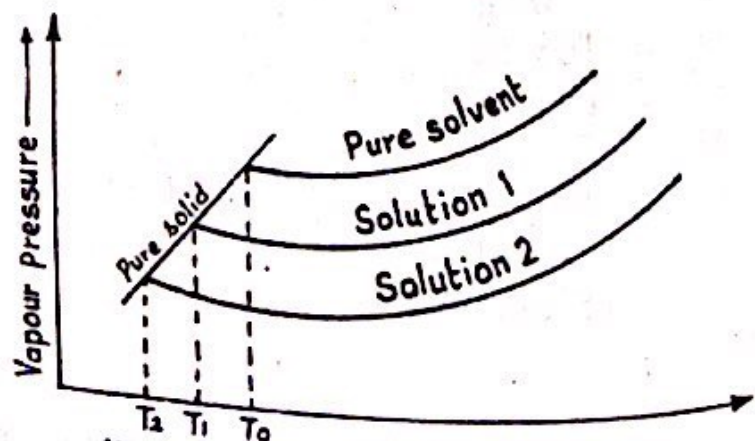
$$M_2 = \frac{4 \times 18 \times 2.802}{50 \times 0.042}$$

The molar mass of phenol

$$= 96 \text{ g mol}^{-1}.$$

Depression of freezing point of a solvent by a solute

Freezing point of a liquid is the temperature at which both liquid and its solid have the same vapour pressure. The solution containing a non volatile solute has a lower vapour pressure than the pure solvent. Therefore the freezing point of the solution is lower than that of the solvent. The difference between the freezing point of the pure solvent and that of its solution is called the freezing point lowering (or) freezing point depression. The freezing point of the solution decreases as the concentration of the solute increases. Fig. 5.2 shows the vapour pressure curves of the pure solvent, the solutions of different concentrations and the solid solvent.



At T_0 , the freezing point of the solvent there is a sharp change in the curve. The vapour pressure - temperature curve below the temperature, T_0 is that for a solid. The freezing point of the solution 1 is T_1 . Dissolving a non volatile solute in a liquid causes a lowering of freezing point. Addition of more solute to form solution 2 causes a further lowering of vapour pressure and the freezing point falls to T_2 .

The lowering of freezing point of a dilute solution is proportional to the lowering of the vapour pressure of the same solution.

Determination of molar mass of solute by freezing point depression method: (Cryoscopic method)

If the freezing point of the solvent is T_0 and that of the solution is T , then the depression of freezing point is given by,

$$T_f = T_0 - T.$$

The depression of freezing point is proportional to the lowering of vapour pressure.

$T_f \propto p_0 - p$ (lowering of vapour pressure) According to Raoult's law,

$$\frac{p_0 - p}{p_0} = x_2 \text{ (mole fraction of the solute)}$$

$$p_0 - p = p_0 x_2$$

$$p_0 - p \propto x_2$$

Therefore,

$$T_f \propto x_2$$

$$T_f = K x_2$$

where K is a proportionality constant.

For a dilute solution,

$$\Delta T_f = K \frac{n_2}{n_1} \left(\because X_2 = \frac{n_2}{n_1} \right)$$

where n_1 is the number of moles of the solvent and n_2 is that of the solute.

$$\Delta T_f = K n_2 \times \frac{M_1}{w_1} \left(\because n_1 = \frac{w_1}{M_1} \right)$$

where w_1 is the mass of the solvent and M_1 is the molar mass of the solvent.

Molality of a solution is defined as the number of moles of the solute per kilogram of the solvent. If the mass of the solvent, w_1 , is taken in kilogram units, n_2/w_1 is equal to the molality, m , of the solution

$$T_f = K M_1 m$$

$$T_f = K_f m$$

where K_f is the new proportionality constant called the molal freezing point depression constant (or) the cryoscopic constant for the solvent. Therefore the

depression of freezing point of a dilute solution is proportional to the molality of the solution.

$$\Delta T_f = \frac{k_f w_2}{M_2 w_1}$$

Freezing point depression = Freezing point constant \times

$$\frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

If the mass of solvent (w_1) is expressed in gram, then

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

The cryoscopic constant may be defined as the depression of freezing point shown by a molar solution. The value of K_f is expressed as degrees / molality or as $K \text{ kg mol}^{-1}$.

$$K_f = \frac{\Delta T_f (K) \times M_2 (\text{g mol}^{-1} \times w_1 \text{ kg})}{W_2 (\text{g})}$$

$$= K \text{ kg mol}^{-1}$$

One mole of a non volatile normal solute in 1 kg of water lowers the freezing point of water by 1.86 K. Therefore the value of K_f for water is 1.86 $K \text{ kg mol}^{-1}$. Each solvent has a characteristic value of K_f . Values of K_f for some of the solvents are given below:

Benzene 5.13 $K \text{ kg mol}^{-1}$

Acetic acid 3.9 $K \text{ kg mol}^{-1}$

Ethyl alcohol 1.99 $K \text{ kg mol}^{-1}$

Determination of freezing point depression

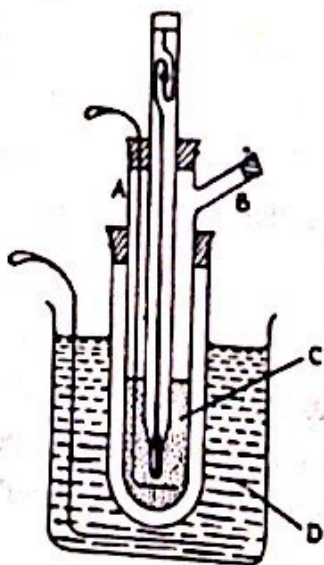


Fig. 5.3.
Beckmann's apparatus - Cryoscopy
C) Solution D) Freezing mixture

The depression of freezing point is determined by Beckmann's method. The apparatus used is shown in Fig. 5.3.

The apparatus consists of an inner glass tube A with a side arm, B. The tube is fitted with a Beckmann thermometer which provides an air jacket. The whole is immersed in a freezing mixture.

A known mass of solvent (w_1) is placed in the inner tube 'A' and stirred gently. The movement of the mercury in the Beckmann thermometer is watched. The temperature recorded on the thermometer drops steadily and reaches a level below that of the true freezing point of the solvent. As the crystallisation of the solvent begins, the temperature raised and remains steady. This steady

temperature (T_0) is recorded as the freezing point of pure solvent.

The tube is taken out of the freezing mixture and the solvent is remelted. A known mass of solute (w_2) is added to the solvent through the side arm, B, and is allowed to dissolve. The freezing point of the resulting solution (T) is determined in the same way as for the pure solvent. The difference between the two freezing points gives the depression of freezing point ($T_0 - T$).

Knowing the mass of the solute (w_2), the mass of the solvent (w_1) in kg, molar mass of the solvent (M_1), and cryoscopic constant (K_f), the molar mass of the solute (M_2) can be calculated.

$$M_2 = \frac{K_f w_2}{\Delta T_f w_1}$$

Beckmann thermometer

Beckmann thermometer is used to measure small temperature changes in the freezing points or the boiling points of the pure solvent and solution. Beckmann thermometer is not used in determining the absolute value of freezing temperature of the solvent or the solution. Temperature differences of 0.01 K can easily be observed. (Fig. 5.4).

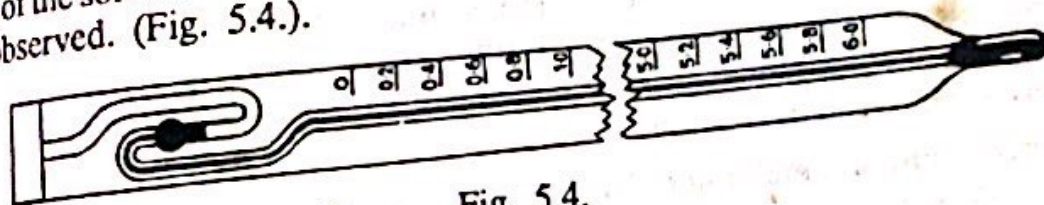


Fig. 5.4.

Beckmann Thermometer

Beckmann thermometer consists of a large thermometer bulb at the bottom of a fine capillary tube and a reservoir of mercury at the top. As the capillary tube is fine, a small change of temperature causes a considerable movement of mercury level in the capillary. The whole scale of a Beckmann thermometer covers only about 6K. The level of mercury in the capillary should be on the reservoir and vice-versa. When the Beckmann thermometer is used at high temperatures some of the mercury from the lower bulb to the upper reservoir. At low temperatures, mercury from the reservoir is brought down into the thermometer bulb.

Elevation of boiling point of a solvent by a solute

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

The solution containing a non volatile solute has a vapour pressure lower than the pure solvent. Therefore, the presence of solute in a liquid is accompanied by a rise in boiling point. The difference between the boiling point of solution and that of solvent is called the elevation of boiling point or boiling point elevation. The elevation of boiling point depends on the concentration of the solution.

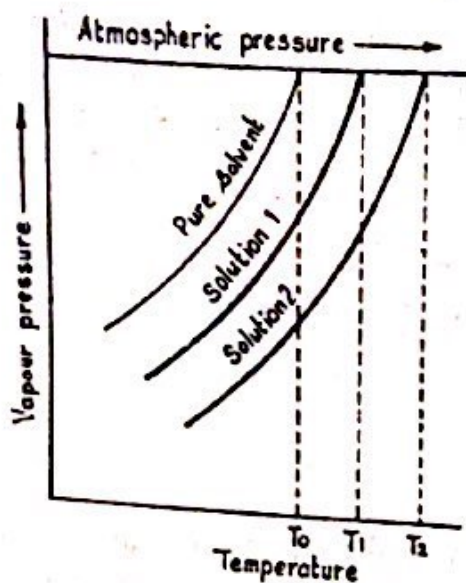


Fig. 5.5.

Vapour pressure temperature curves (boiling point) for solvent and solutions.

elevation of boiling point (T_2). A lowering of vapour pressure causes and elevation of boiling point.

Determination of molar mass by elevation of boiling point method (Ebullioscopic method)

If the boiling point of the solvent is T_0 and that of the solution is T , then the elevation of boiling point is given by, $T_b = T - T_0$. The elevation of boiling point is proportional to the lowering of vapour pressure.

According to Raoult's law,

$$\frac{p_0 - p}{p_0} = x_2 \text{ (mole fraction of the solute)}$$

$$p_0 - p = p_0 x_2$$

$$p_0 - p \propto x_2$$

Therefore,

$$\frac{T_b}{T_b} \propto \frac{x_2}{x_2}$$

$$T_b = K x_2$$

where K is a proportionality constant. For a dilute solution,

$$\Delta T_b = K \frac{n_2}{n_1} \left(\because x_2 = \frac{n_2}{n_1} \right)$$

where n_1 is the number of moles of the solvent and n_2 is that of the solute.

$$\Delta T_b = K n_2 \frac{M_1}{w_1} \left(\because n_1 = \frac{w_1}{M_1} \right)$$

The relationship between lowering of vapour pressure and elevation of boiling point is shown in Fig. 5.5.

When the vapour pressure reaches the atmospheric pressure the solvent boils, so that the boiling point of the pure solvent is T_0 . A solute dissolved in the solvent gives solution, (1), with a lower vapour pressure. The vapour pressure of the solution increases with rise of temperature. When the vapour pressure reaches the atmospheric pressure, the solution boils at the temperature, T_1 . The boiling point of the solution (1), T_1 , is higher than the boiling point, T_0 , of the pure liquid. Dissolving a non volatile solute in a solvent causes an elevation of boiling point. Addition of more solute to form solution (2), causes a further lowering of vapour pressure of the solution

where w_1 is the mass of the solvent and M_1 is the molar mass of the solvent. Molality of a solution is defined as the number of moles of the solute per kilogram of the solvent. If w_1 is taken in kilogram units n_2/w_1 is equal to the molality, m , of the solution.

$$T_b = K M_1 m$$

$$T_b = K_b m$$

where K_b is the new proportionality constant called molal elevation constant (or) ebullioscopic constant.

$$\Delta T_b = \frac{K_b w_2}{M_2 w_1} \left(\text{where } m = \frac{w_2}{M_2 w_1} \right)$$

\therefore Elevation of boiling point,

$$= \text{Ebullioscopic constant} \times \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

If the mass of solvent (w_1) is expressed in gram, then

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

The ebullioscopic constant may be defined as the elevation of boiling point shown by a molal solution.

The value of K_b is expressed as degrees/molality or $K \text{ kg mol}^{-1}$. The elevation produced by one mole of solute in 1 kg of water is 0.52 K . Therefore the value of K_b for water is $0.52 \text{ K kg mol}^{-1}$.

Values of K_b for some of the solvents are given below:

Benzene	$2.53 \text{ K kg mol}^{-1}$
Acetic acid	2.93
Ethyl alcohol	1.20

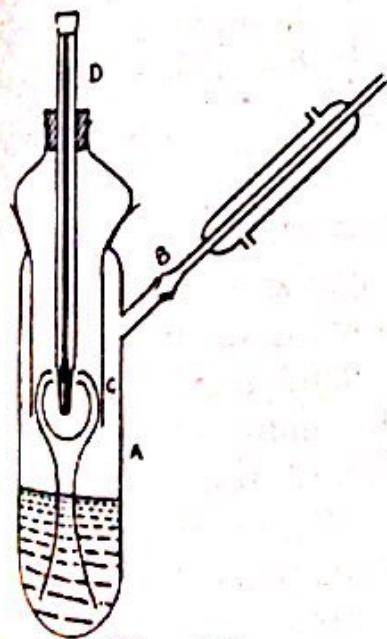


Fig. 5.6.
Cottrell's method - ebullioscopy

Determination of elevation of boiling point

The elevation of boiling point is determined by Cottrell's method. The apparatus used is shown in Fig. 5.6.

A is the boiling tube in which the experimental liquid is taken. A thick platinum wire is fused at the bottom of the tube. This ensures uniform boiling of the liquid. The side tube B, is connected to a condenser. C is a sheath that prevents the cold condensate from reaching the Beckmann thermometer, D. The tube is heated by a small flame. The vapour and the boiling liquid are sprayed on the bulb of the Beckmann thermometer after passing

through the inverted funnel. A known mass of the solvent (w_1) is taken in the boiling tube. The boiling point (T_0) is recorded on the thermometer, when the reading is steady. After cooling, a known mass (w_2) of the solute is added. The boiling point of the solution (T) is measured. The difference of temperature ($T - T_0 = \Delta T_b$) gives the elevation of boiling point.

Knowing the mass of the solute (w_2) the mass of the solvent (w_1) in kg, molar mass of the solvent (M_1) and ebullioscopic constant (K_b), the molar mass of the solute (M_2) can be calculated.

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

Osmosis and osmotic pressure:

When two solutions are separated by a semi permeable membrane, solvent passes from the more dilute solution to the more concentrated. This phenomenon is called osmosis. When a semi-permeable membrane separates a solvent from a solution, solvent molecules tend to pass from the solvent side into the solution. A semi permeable membrane is a film of material which can be penetrated by a solvent but not by a solute. Many natural membranes act as semi-permeable membranes and substances such as copper (II) hexacyanoferrate (II) ($\text{Cu}_2[\text{F}_3(\text{CN})_6]$), parchment paper and cellophane are also semi permeable. The following examples illustrate the action of semipermeable membranes in osmosis.

a) The outer shell of an egg can be removed by dissolving in hydrochloric acid. If the egg is placed in water, it swells. If it is placed in strong brine, shrinks. The membrane beneath the outer shell of the egg acts as a semi permeable membrane.

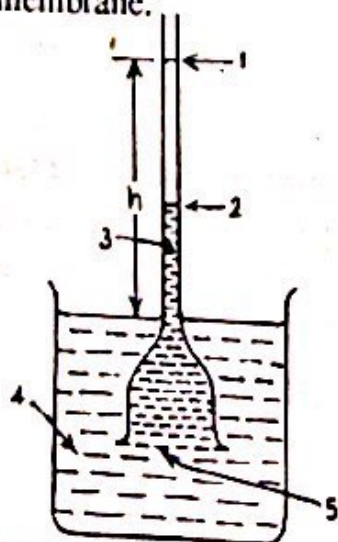


Fig. 5.7. Osmosis - apparatus for demonstration

- 1) Final level
- 2) Original level
- 3) solution of Sugar
- 4) Water
- 5) Semi permeable membrane

b) If an animal bladder, eg., a pig's bladder, is filled with ethanol and tied at the neck, it will swell when immersed in water and finally burst. This is because water diffuses through the animal bladder much more rapidly than ethanol diffuses out.

Osmosis can be demonstrated by a simple apparatus shown in Fig. 5.7.

A thistle funnel is covered with a semi-permeable membrane. A sugar solution is taken in it and the thistle funnel is immersed in water. Water enters through the semi-permeable membrane into the funnel due to osmosis so that the level of liquid in the thistle funnel rises. As the level of the liquid in the funnel rises, the water that has already entered the solution creates some additional pressure and opposes the inflow of water. Thus, with time the rate of flow of solvent to the solution decreases until an equilibrium is established.

ished and no further osmosis takes place. This hydrostatic pressure, which just prevents the passage of solvent into the solution through a semi permeable membrane is called osmotic pressure of the solution. Osmotic pressure may also be defined as the pressure required to prevent the osmosis when the solution is separated from pure solvent by a semi permeable membrane.

Measurement of Osmotic pressure

The osmotic pressure of a solution is measured by Berkeley and Hartley's method. The apparatus used is shown diagrammatically.

The apparatus consists of a porous pot containing copper ferrocyanide deposited in its walls. The porous pot is fitted into a steel vessel to which is fitted a

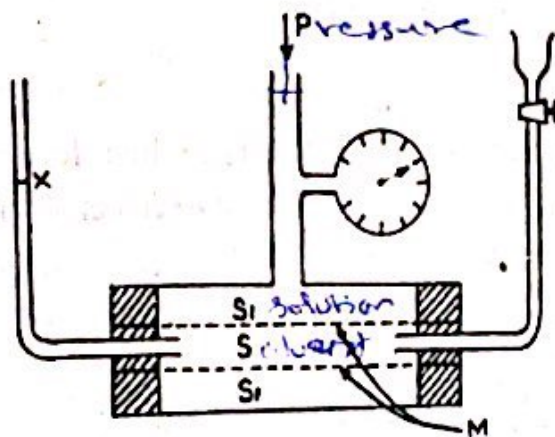


Fig. 5.8.

Berkeley and Hartley's apparatus for determination of osmotic pressure.

piston for the application of pressure and a gauge for the measurement of pressure. Two ends of the porous pot are closed with stoppers with a capillary tube and solvent reservoir on either side.

Water is taken in the porous pot and the steel vessel with the solution. Water in the porous pot tends to pass into the solution through the membrane. As a result the level in the capillary indicator moves downwards. External pressure is now applied by the piston to the solution so that the level in the capillary indicator remains stationary. This pressure is measured on the pressure gauge. The pressure recorded at equilibrium gives the osmotic pressure of the solution at the temperature of the experiment.

Laws of osmotic pressure

Van't Hoff showed that the dilute solutions behave like ideal gases. The relationship of osmotic pressure with concentration and temperature is the same as that of gaseous pressure with concentration and temperature. The following laws were deduced by van't Hoff for dilute solutions.

- (1) At a given temperature, in dilute solution the osmotic pressure of a solution is directly proportional to its concentration;
Osmotic pressure (Π) \propto c (concentration of solution)

$$\left(\text{where } C = \frac{\text{mole}}{\text{volume}} \right)$$

The relationship can be written as,

$$\pi \propto \frac{1}{V(\text{Volume of solution})} \text{ (for a given mass of solute) or } \pi V = \text{a constant}$$

This is analogous to the statement of Boyle's law. This law is therefore known as van't Hoff-Boyle's law of dilute solutions.

(2) The osmotic pressure of a solution of given concentration is directly proportional to the absolute temperature.

$$\pi \propto T \text{ (absolute temperature)}$$

$$\frac{\pi}{T} = \text{a constant.}$$

This is analogous to Charles's law. This law is therefore known as van't Hoff-Charles's law of dilute solutions. Combining the effects of volume of solution and absolute temperature on the osmotic pressure,

$$\pi \propto \frac{T}{V}$$

$$\pi = \frac{kT}{V} \text{ where } k \text{ is a constant.}$$

$$\pi V = kT$$

If 1 mole of the solute is considered the relationship becomes

$$\pi V = RT$$

where R is a constant known as van't Hoff constant. The numerical value of R is the same as that in the gas equation.

If the number of moles of the solute is n mol, the relationship becomes

$$\pi V = nRT$$

(3) There is a remarkable similarity between the behaviour of molecules distributed throughout a gas and the solute distributed throughout a solution. The osmotic pressure of a dilute solution, in fact, is equal to the pressure which the solute would exert if it existed as a gas at the same temperature occupying a volume equal to that of the solution.

At a given temperature, solutions having equal molar concentration of different solutes have the same osmotic pressure. If two solutions have the same osmotic pressure, the solution are said to be isotonic.

(4) 1 mol of a solute dissolved in 22.4 dm³ of solution at 273 K will exert an osmotic pressure of 1.013 × 10⁵ N m⁻².

Determination of molar mass of solute from osmotic pressure measurement.

Like vapour pressure, freezing point depression and boiling point elevation

The osmotic property also depends on the total number of solute particles dissolved in a solution. Measurement of osmotic pressure can be used to calculate the molar masses of solutes.

$$\pi V = n RT$$

If w g of non volatile solute of molar mass M is present in V dm³ of solution then

$$n = \frac{W}{M}$$

$$\pi V = \frac{W}{M} RT$$

$$M = \frac{W RT}{\pi V}$$

The value of $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

w , T , and V are measurable quantities, Hence, M can be found out.

Abnormal molar masses

The colligative properties such as lowering of vapour pressure, depression of freezing point, elevation of boiling point and osmotic pressure are used to determine molar masses. The relationships used for the determination are valid only for ideal solutions which obey Raoult's law. If there is deviation from ideal behaviour, the molar masses determined by using the above colligative properties do not agree with the normal values. If the number of particles increases through dissociation of the solute, the observed colligative property increases. If association occurs, the number of particles is less than the expected hence the colligative property is also less than the expected.

Vant' Hoff introduced a factor, i known as van't Hoff factor to express the extent of dissociation or association.

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

Electrolytes give abnormally high values of colligative properties. The reason for the high value of i for electrolytes is dissociation of solute into ions. If a solute, such as NaCl , is completely dissociated, there are two moles of ions for every mole of NaCl . Therefore, the colligative properties are twice the values calculated in the absence of ionisation. If copper (II) nitrate, $\text{Cu}(\text{NO}_3)_2$ is completely dissociated, there are three moles of ions for every one mole of $\text{Cu}(\text{NO}_3)_2$. Therefore, the colligative properties are three times the values calculated. The measured experimental value of molar mass will be less than the normal value.

In case of association, values of i will be less than unity. Association of solute molecules in a solution is generally caused by hydrogen bonding between the solute molecules. The molecules such as alcohols, phenols, carboxylic acids are capable of forming hydrogen bonds and getting associated. When benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is dissolved in benzene, the experimental value of molar mass is