SOLUTIONS

Binary Solution!
miscible?
Solute?
Solvent?

8.1.0 INTRODUCTION

"A solution is a homogeneous mixture of two or more substances existing in one or more states." That solution which is consisted of two components is called a binary solution. That component which has the same physical state as that of solution is called solvent. Mostly it is thought that the substance in greater quantity is called solvent and the other component is called solute.

In a dilute solution, the quantity of the solute is very small as compared to that of solvent.

There are various types of solutions depending upon the fact that out of three states of matter which is solute and which of them is the solvent.

8.1.1 Concentration units of solutions:

The concentration of a solution tells us quantity of solute dissolved in a given quantity of solvent or solution. These various units are as follows:

1. **Strength of solution:** It is the number of grams of solute present in one dm^3 of solution.

2. **% age of solution:** The % age of solution can be (a) weight / weight (b) weight / volume (c) volume / weight (d) volume / volume.
   It is the % age by mass or by volume per 100 parts of the solution.

3. **Molarity.** It is the number of moles of the solute dm^{-3} of solution.

4. **Molality.** It is the number of moles of the solute per 1000 grams of solvent.

5. **Normality:** It is the number of gram equivalents of the solute dm^{-3} of solution.

6. **Mole fraction:** It is the number of moles of any component divided by total number of moles of all the components of the solution. It is always less than unity.

7. **Parts per million:** It is the number of parts of a component per million parts of the solution. It is abbreviated as ppm

$$\text{ppm of a component} = \frac{\text{Mass of the component}}{\text{Total mass}} \times 10^6$$

This unit is used for those solutions in which the quantity of the solute is extremely small.

8.1.2 Formulas for various concentration units of solutions:

(1)   **% age composition:**

    (a)   **Weight/weight % age:** 5 grams of glucose is dissolved in 100 grams of solutions. (5 g of solute + 95 g of solvent).

    (b)   **Weight/volume % age:** 5 grams of glucose is dissolved in 100 cm³ of solution.

    (c)   **Volume/weight % age:** 5 cm³ of ethyl alcohol is dissolved in 100 g of solution.

    (d)   **Volume / volume % age:** 5 cm³ of ethyl alcohol is dissolved in 100 cm³ of solution.

    It means that the total volume or weight of the solution is 100 units. It may be mass in grams or volume in cm³.

(2)   **Molarity:**

Molarity of solution is related with mass of the solute, molar mass of the solute and volume of the total solution:

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

(3)   **Molality:**

Molality of a solution is related with mass of the solute, molar mass of solute and mass of the solvent

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

(4)   **Normality:**

Normality of a solution is related with mass of the solute, equivalent mass of the solute and volume of the solution in dm³.

$$\text{Normality} = \frac{\text{Mass of solute}}{\text{Equivalent mass of solute}} \times \frac{1}{\text{Volume of solution in } dm^3}$$

(5)   **Mole fraction:**

"It is the ratio of number of moles of one component to the total number of moles of all the components of solution."

Suppose, there are three components 'A', 'B' and 'C' having number of moles 'n_A', 'n_B' and 'n_C'. The mole fractions are denoted by 'x_A', 'x_B' and 'x_C'.

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

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

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

The sum of mole fractions is unity

$$x_A + x_B + x_C = 1$$

8.2.0 SOLUTION OF COMPLETELY MISCIBLE LIQUIDS

To have the solutions of this category, we have to take both polar liquids or both non-polar ones. When such liquids are mixed, they form only one phase.

8.2.1 Types of completely miscible solutions:

Completely miscible solutions form two types of solutions:

(i)   Ideal solution.

(ii) None-ideal solution.

Now let us discuss them one by one.

8.2.2 Ideal solution:

In order to differentiate between ideal and non-ideal solutions, some of the following criterias are taken into consideration.

(i)   If the forces of interaction of the components after mixing are same as among the molecules of pure components, then the solutions are ideal.

(ii) If the heat of solution is zero, then the solution is ideal.

(iii) If there is no change in the volume of the solution, then the solution is ideal.

(iv) If the equation of osmatic pressure is obeyed by the solutions, then they behave as ideal solutions i.e.

$$\pi V = n_2 RT$$

(v)   Those solutions which obey the Raoult's law at all concentrations and all the temperatures, then they are called ideal solution.

8.2.3 Best criteria of ideality of a solution:

Raoult's law is one of the best criteria to check, whether a solution is ideal or not. So, in order to understand the difference between an ideal and non-ideal solution, let us thoroughly understand the Raoult's law.

8.3.0 RAOULT'S LAW

8.3.1 Introduction:

We know that vapour pressure is one of the basic properties of a liquid. It increases with the increase of temperature. When solutes are added into the solvents, then their vapour pressures are lowered. This lowering of vapour pressure is due to the presence of the particles of the solute on the surface of solutions. Raoult has given the quantitative relationship between vapour pressure of the solution and the quantities of the solutes and the solvents.

8.3.2 Raoult's law when the solute is non-volatile, non-electrolyte:

Let us consider that, the vapour pressure of the pure solvent is P°, and that of the solution is P.

Let the mole fraction of solvent and the solute be 'X_1' and 'X_2' respectively.

According to first definition of Raoult's law, "the vapour pressure of the solution is directly proportional to the mole fraction of the solvent."

$$P \, \alpha \, X_1$$
$$P = P°X_1 \qquad \cdots\cdots (1)$$

Since,

$$X_1 + X_2 = 1$$
$$X_1 = 1 - X_2 \qquad \cdots\cdots (2)$$

Putting the value of 'X_1' in equation (1)

$$P = P° (1 - X_2)$$
$$P = P° - P°X_2$$
$$P° - P = P°X_2$$
$$\Delta P = P°X_2 \qquad \cdots\cdots (3)$$
$$\Delta P \, \alpha \, X_2$$

So, "the lowering of vapour pressure 'ΔP' is directly proportional to the mole fraction of the solute". This is, you can say the second definition of Raoult's law.

$$\frac{\Delta P}{P°} = X_2 \qquad \cdots\cdots (4)$$

$\frac{\Delta P}{P°}$ is called relative lowering of vapour pressure.

According to third definition of Raoult's law "the relative lowering of vapour pressure is equal to mole fraction of the solute".

8.3.3 Importance of relative lowering of vapour pressure:

According to third definition of Raoult's law, given in equation (4), we feel that it should be better reported in the literature, rather than lowering of vapour pressure. Relative lowering of vapour pressure is

(a)   Independent of temperature.

(b)   Proportional to the concentration of the solute.

(c)   Is a constant quantity, when equimolecular proportions of different solutes are dissolved in same mass of the same solvent.

EXAMPLE (1)

A solution of sugar is prepared in water at 25°C. The vapour pressure of pure water is 17.51 torr and is decreased by 0.0614 torr. Calculate (a) relative lowering in vapour pressure of the solution (b) vapour pressure of solution (c) mole fractions of water and sugar.

SOLUTION:

Data:

Vapour pressure of water, ($P°$) = 17.51 torr

Lowering of vapour pressure, (ΔP) = 0.0614 torr

Formula:

(a)   Relative lowering in vapour pressure
$$= \frac{\Delta P \text{ torr.}}{P° \text{ torr.}}$$
$$= \frac{0.0614}{17.51} = 0.00351$$

[handwritten marginal notes:]
where :
P = Solution
P° = Pure Solvent = P. Short
X_1/X_1 = Solvent
X_2/X_0 = Solute

Relative lowering of vapour pressure

(b) Vapour pressure of solution, P_s = vapour pressure of solvent
$$- \text{lowering of V.P.}$$
$$= 17.51 - 0.0614$$
$$= 17.44\,86 \text{ torr}$$

(c) We know that , $\dfrac{\Delta P}{P^o} = X_{solute} = 0.00351$

So, Mole fraction of sugar $= 0.00351$

Since the sum of mole fractions of a solution is unity.

So,

Mole fraction of water as a solvent $= 1 - 0.00351 = \boxed{0.99649}$ Ans.

8.3.4 Raoult's law when both components are volatile:

Under these circumstances, let us have two volatile liquids 'A' and 'B', having vapour pressures in the pure states as $'P^o_A'$ and $'P^o_B'$. After mixing the vapour pressures of both the components are changed. Suppose their vapour pressures in the solution states or $'P_A'$ and $'P_B'$. These vapour pressures are lower than $'P^o_A'$ and $'P^o_B'$ respectively. If mole fraction of the both components are denoted by $'X_A'$ and $'X_B'$ then, we can apply the first definition of Raoult's law on both components:

$$P_A = P^o_A X_A$$
$$P_B = P^o_B X_B$$

The total vapour pressure of the solution is the sum of these vapour pressures $'P_A'$ and $'P_B'$.

$$P_t = P_A + P_B$$
$$P_t = P^o_A X_A + P^o_B X_B \qquad \dotsb (5)$$

In order to make this equation (5) more useful, let us have only one mole fraction of one component

Since, $X_A + X_B = 1$

So, $X_B = 1 - X_A \qquad \dotsb (6)$

Putting equation (6) into equation (5)

$$P_t = P^o_B(1 - X_A) + P^o_A X_A$$
$$P_t = P^o_B - P^o_B X_A + P^o_A X_A$$
$$P_t = P^o_B + (P^o_A - P^o_B)X_A$$
$$P_t = (P^o_A - P^o_B) X_A + P^o_B \qquad \dotsb (7)$$

Equation (7), tell us that the total vapour pressure $'P_t'$ of the solution depends upon the vapour pressure of pure component and mole fraction of the component 'A', at a given temperature. The values of $'P^o_A'$ and $'P^o_B'$ are constants.

Hence, the value of the total vapour pressure P_t', depends upon the mole fraction of the component 'A'. Keep it in mind that, when the mole fraction of components 'A' changes then that of 'B' also changes. It means the mole fractions of both 'A' and 'B' control the total vapour pressure, P_t'.

8.3.5 Graphical explanation of Raoult's law:

Equation (7) is the equation of a straight line. 'X_A' is the independent variable, while 'P_t'' is the dependent variable. If a graph is plotted between 'X_A' on x-axis and 'P_t'' on y-axis, then a straight line is obtained as shown in the following diagram (1).   (See page 583 11.2.0 Idea of straight line).

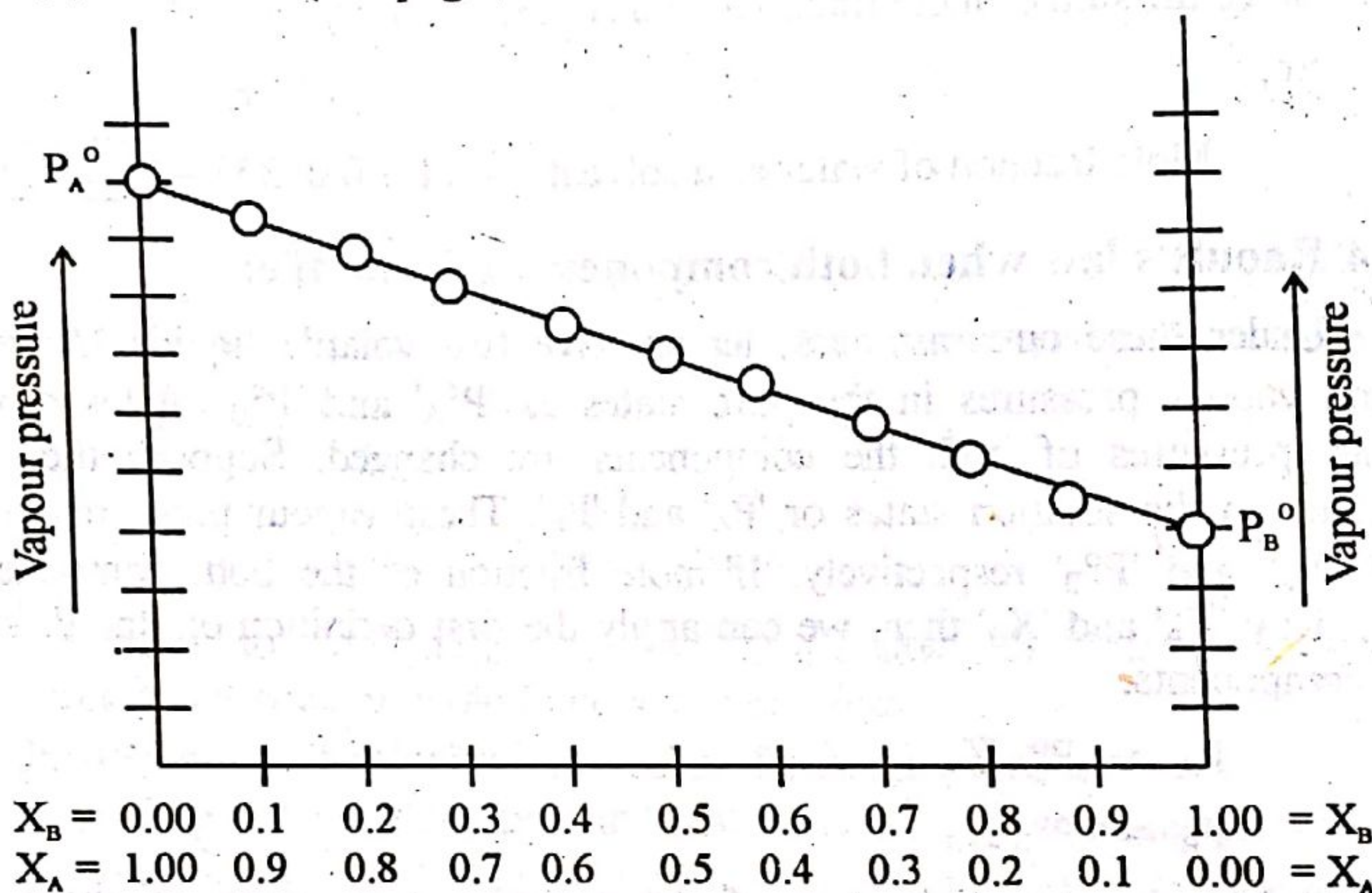| X_B = | 0.00 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.00 | = X_B |
| X_A = | 1.00 | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 | 0.4 | 0.3 | 0.2 | 0.1 | 0.00 | = X_A |

Fig. (1) Composition / vapour pressure graph for Raoult's Law.

According to this graphical representation component 'A' is more volatile as compared to 'B'. So, the vapour pressure of component 'A' in the pure state '$P°_A$' is greater than that of '$P°_B$' at a given temperature. Remember that we only get the straight line, if all the solutions are ideal.

Individual vapour pressures:

Above graph has been obtained, when we have prepared various solutions and their vapour pressures have been accurately measured, along with the vapour pressures of the pure components.

Each solution which has been prepared, has a total vapour pressure 'P_t' which is due to the both components.

If we want to look at the relative contributions, of 'A' and 'B', towards the total vapour pressure P_t, then we should draw, two hypothetical dotted straight lines as shown in the following diagram (2).
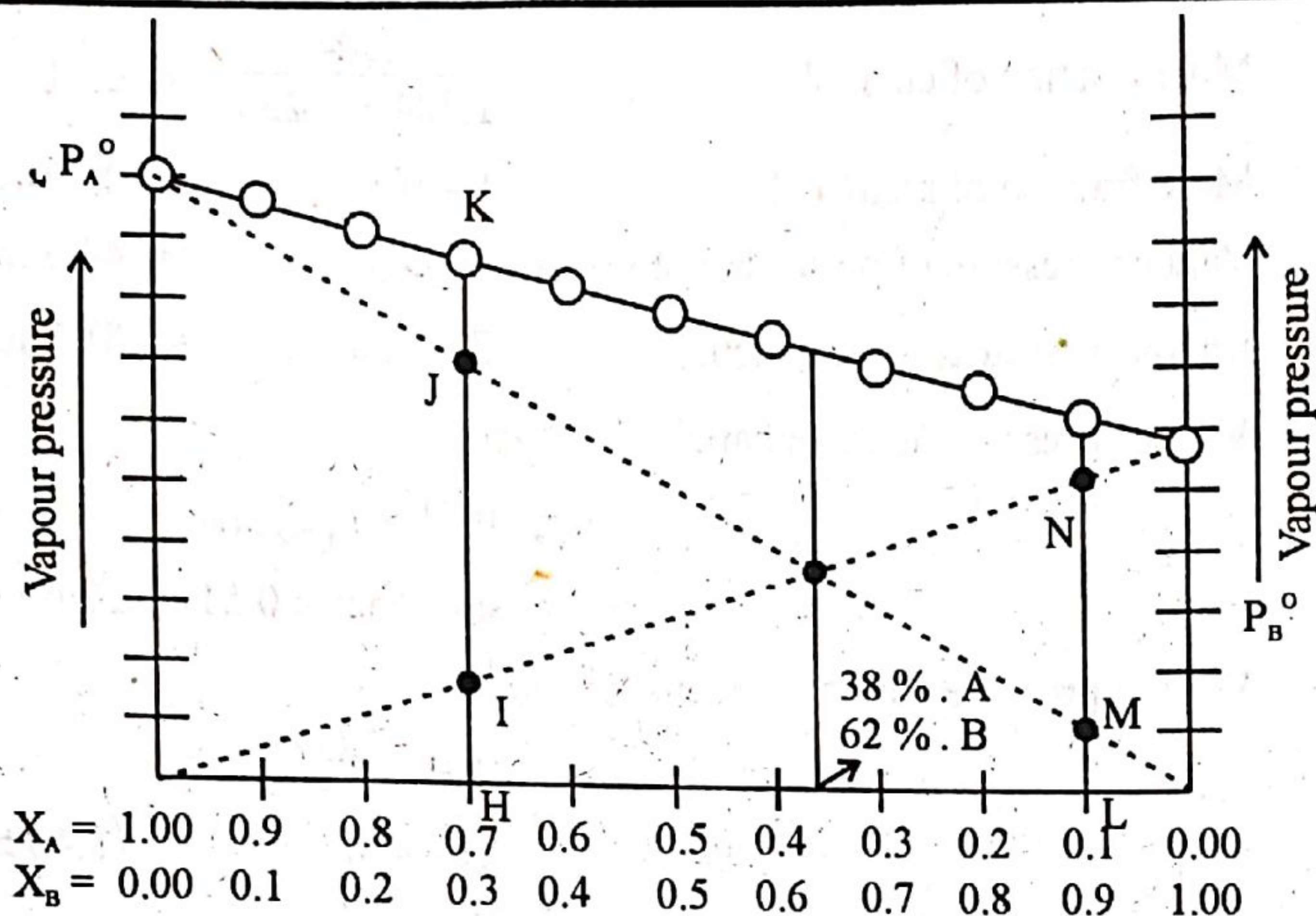
Fig. (2) Determination of compositions for various vapour pressure. of solutions.

When the solution is of 30 % 'B' and 70 % 'A', then the contribution of components. 'A' is 'JH' and that of component 'B' is 'HI'. Similarly, the solution having 90 % 'B' and 10 % 'A', has contribution of component 'A' as 'LM' and that of component 'B' as 'LN'.

If we want to see, that which composition will have 50 % contribution of 'A' and 50 % of 'B', then we should look at that point at which the two dotted lines are crossing each other. It is clear from the graph that, 62 % components 'B' and 38 % 'A' will have fifty fifty contribution towards the total vapour pressure. The reason is that component 'A' is more volatile and its 38 % contribution in the solution state has greater contribution towards vapours and equalizes to 62 % 'B'.

EXAMPLE (2)

An ideal solution of ethanol and methanol is formed at the certain temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of both in vapours. The vapour pressure of ethanol is 44.5 torr and that of methanol is 88.7 torr. at same temperature in the pure slate.

SOLUTION:

Data:

Mass of ethanol $= 60$ g   Molar mass of ethanol $= 46$ g mol^{-1}

Mass of methanol $= 40$ g   Molar mass of methanol $= 32$ g mol^{-1}

Moles of ethanol $= \dfrac{60 \text{ g}}{46 \text{ g}} = 1.304$

Moles of methanol $= \dfrac{40 \text{ g}}{32 \text{ g}} = 1.250$

Mole fraction of ethanol $= \dfrac{1.304}{1.304 + 1.250} = 0.51$

Mole fraction of methanol $= 1 - 0.51 \qquad = 0.49$

Vapour pressure of pure ethanol $= P^\circ_{C_2H_5OH} \qquad = 44.5$ mm

Vapour pressure of pure methanol, $= P^\circ_{CH_3OH} \qquad = 88.7$ mm

Vapour pressure due to ethanol $(P^\circ_{C_2H_5OH})$

$$= 0.51 \times P^\circ_{C_2H_5OH}$$

$$= 44.5 \text{ mm} \times 0.51 = 22.69 \text{ mm}$$

Vapour pressure due to methanol, (P_{CH_3OH})

$$= 0.49 \times P^\circ_{CH_3OH}$$

$$= 887 \text{ mm} \times 0.49 = 43.46 \text{ mm}$$

Total vapour pressure $= P_{C_2H_5OH} + P_{CH_3OH}$

$$= 22.69 \text{ mm} + 43.46 \text{ mm}$$

$$= 66.15 \text{ mm}$$

Mole fraction of methanol in the vapour state

$$= \dfrac{P_{CH_3OH}}{\text{total vapour pressure}}$$

$$= \dfrac{43.46 \text{ mm}}{66.15 \text{ mm}} = 0.657$$

Mole fraction of ethanol in the vapour state $= \dfrac{22.69}{66.15} = \boxed{0.343}$ **Ans.**

8.4.0 FRACTIONAL DISTILLATION

Distillation is the process of separation of two miscible liquids which have difference of boiling points and they are distilled repeatedly.

We are going to discuss the fractional distillation of those pairs of liquids which have made the ideal solutions. Remember that in the case of ideal solutions we will get a straight line for the plot of vapour pressure and composition.

In order to have idea of fractional distillation, we should plot a graph between mole fraction or mole percentage and the temperature. As the diagram shows, that we get two curves rather than a straight line. The upper curve is for the vapours of 'A' and 'B' and the lower curve is for solutions of 'A' and 'B'.

Since 'A' is more volatile than 'B'. So, the boiling point of pure 'A' is less than that of 'B'. We get two curves due to the reason that the composition of the solution and the composition of vapours are different from each other at any temperature. This property of two liquids 'A' and 'B', to show different compositions in liquid and vapour state helps us to separate the two liquids.
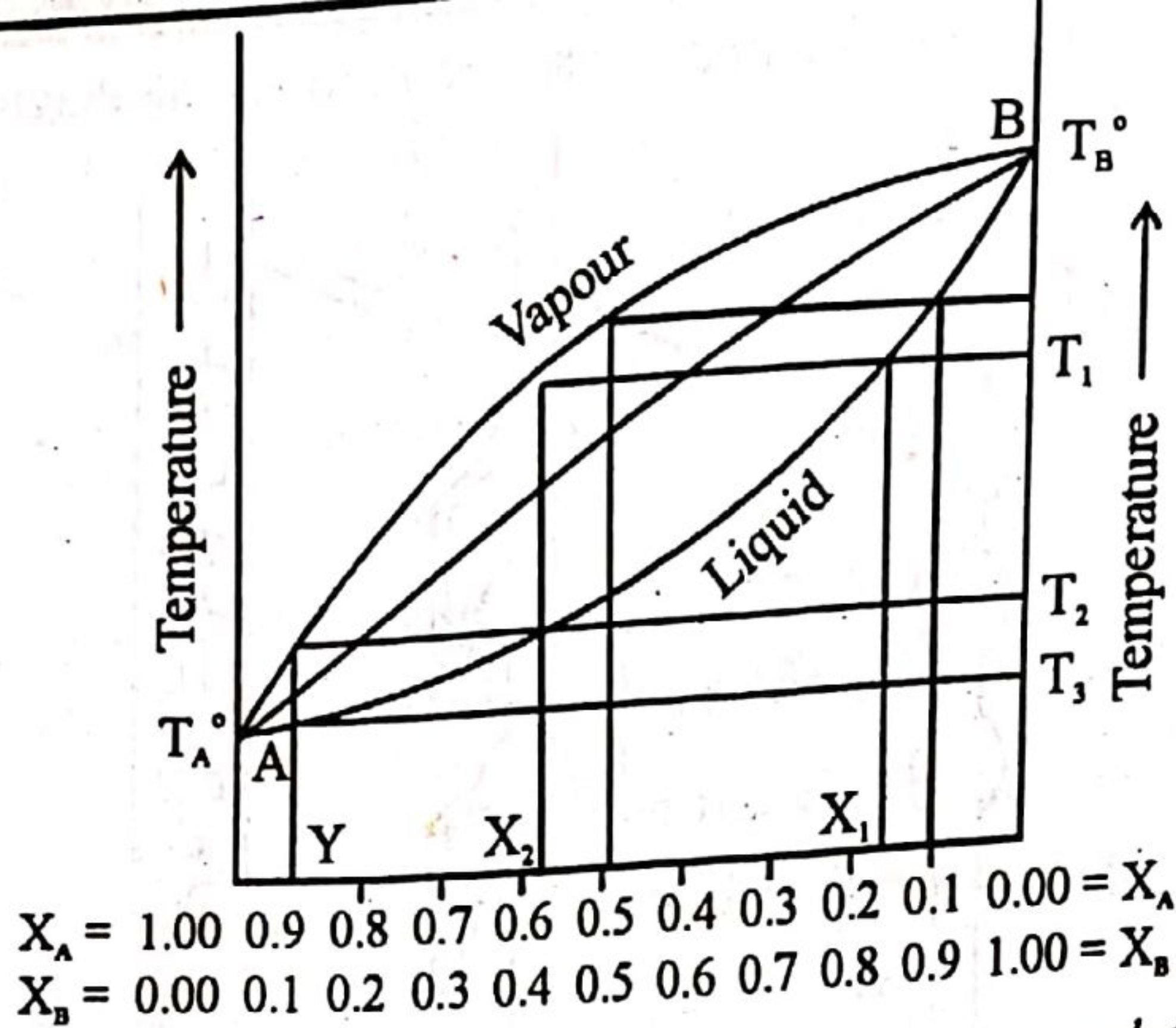
Fig. (3) Composition temperature graph for a binary solution.

According to the above diagram (3), the curve 'AB' shows a change of boiling point with composition. Suppose that at temperature 'T_1', the composition of the solution is 'X_1' that is 17 % A and 83 % B. Since 'A' is more volatile liquid than 'B' so, the vapours at the surface of this solution having composition 'X_1', will have greater % age of 'A' than the % age of 'A' in the solution state. The composition of vapours at this temperature is 58 % A and 42 % B represented by 'X_2'.

When this solution of composition 'X_2' is boiled at temperature 'T_2', then more vapours of the compound 'A' are formed at temperature 'T_2'. The remaining liquid will be richer in 'B', represented by the point 'Y'. The liquid of the composition 'Y' will boil at 'T_3'. At 'T_3' the vapours formed will be again richer in 'A'. It means that the composition of residual liquid will be richer in 'B'.

When the vapours from the liquid mixture at temperature 'T_1' are cooled to room temperature and is distilled again, it will boil at temperature 'T_2' and its composition will be represented by 'Y'. This composition represented by 'Y' will be richer in 'A', than 'B'. The vapours on cooling will give second distillate and will have more of 'A' than in the first distillate.

When we continue this process of condensing the distillate and redistilling is continued as well, then we get the pure component 'A' in the receiving flask in the long run.

When he process of heating and boiling continues, then the boiling point of residual liquid i.e. left behind in the flask will rise up to the point 'B'. This is the boiling point of pure components 'B'. Such liquid solutions will have greater boiling point than T_1.

8.4.1 Process of fractional distillation:

If we want to do the separation of liquid from a binary mixture, then it can be done in single operation, subject to the conditions that solution is ideal. Moreover, we have to use the fractionating column.

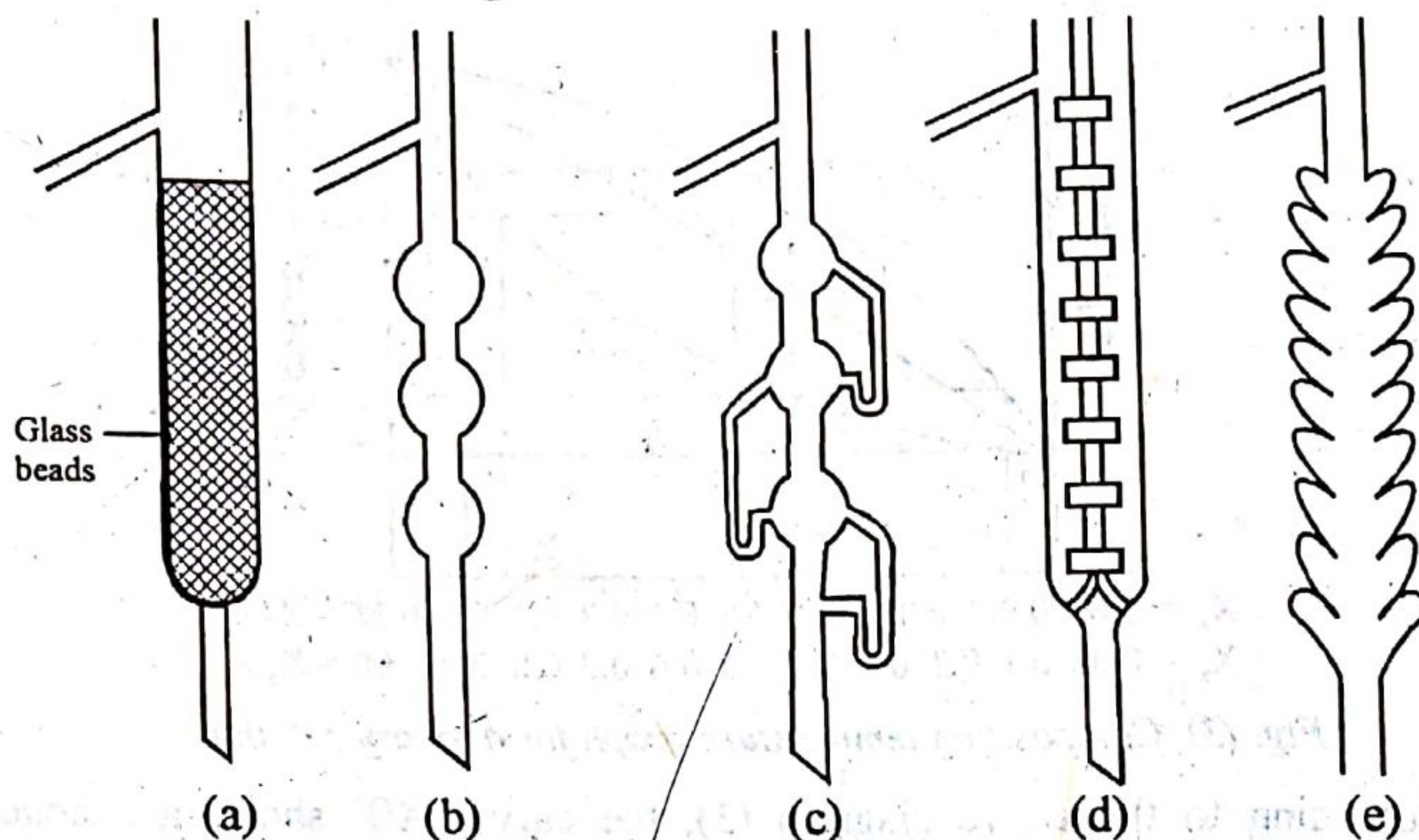The various fractionating columns are shown in following diagram (4).

Fig. (4) Various fractionating columns mostly used in laboratories.

Fractionating column is fitted with the thermometer. This is again fitted on a round bottomed flask as shown in the following diagram (5).
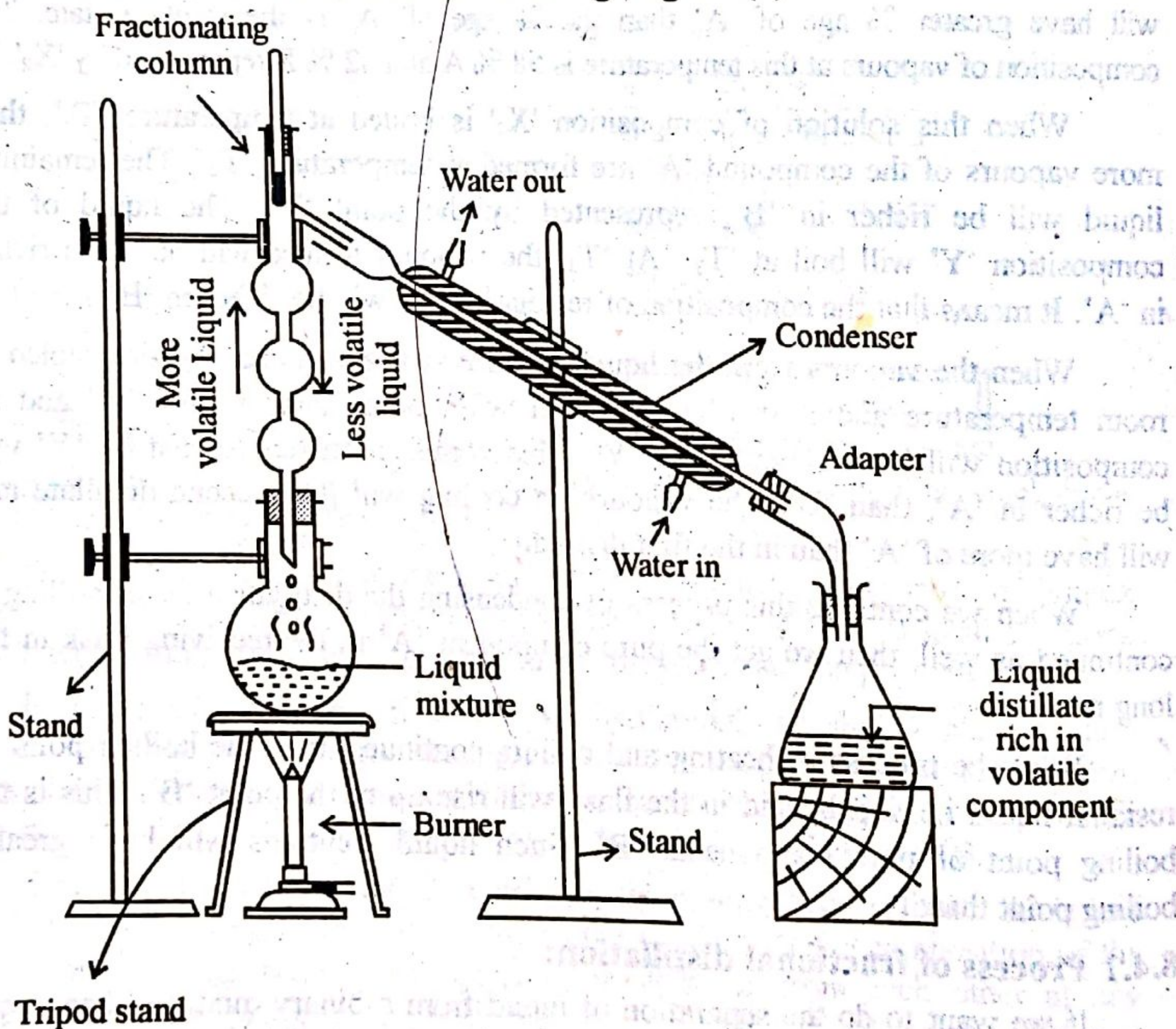

Fig. (5) Fractional distillation by using fractionating column.

The pair of liquids which are to be separated is heated in the round bottomed flask. The more volatile component 'A' will rise up in the form of vapours in the column. But keep it in mind that, a small amount of vapours of component 'B' will also rise. When the vapours rise up in the fractionating column, then partial condensation takes place and the liquid flows down. The condensation of the vapours of 'B' take place more readily, than that of 'A'. The liquid which comes back in the round bottom flask becomes richer in 'B'.

Those vapours which go up and transfer to the receiving flask are richer in 'A'. This process continues and in the long run, we get pure component 'A' in receiving flask and pure 'B' in the distillation flask.

8.4.2 Non-ideal Solutions:

No doubt, there are certain pairs of miscible liquids which obey the Raoult's law throughout the complete range of concentrations at a given temperature. These pairs are as follows.

(i) Benzene and bromobenzene

(ii) Benzene and ethylenedichloride

(iii) Ethylene dibromide and propylenedibromide

However, there are many systems of pairs of liquids, which do not obey the Raoult's law, to a greater or lesser extent. It depends upon the nature of the liquids and the temperature.

In order to understand the deviations of the solution from Raoult's law, let us understand the graphs between mole fractions and vapour pressures. We observe that there are three types of solutions which show non-ideal behaviours and they show deviations from Raoult's law.

TYPE-I:

Those pairs of liquids, whose total vapour pressures are intermediate between those of pure constituents:

(a) If we plot a graph between compositions and vapour pressures for cyclohexane and CCl_4 system, then we observe that the graphs pass above the expected straight line of Raoult's law. Anyhow, the total vapour pressure is all the times intermediate between the vapour pressures of two components. The following diagram (6) makes the idea clear.
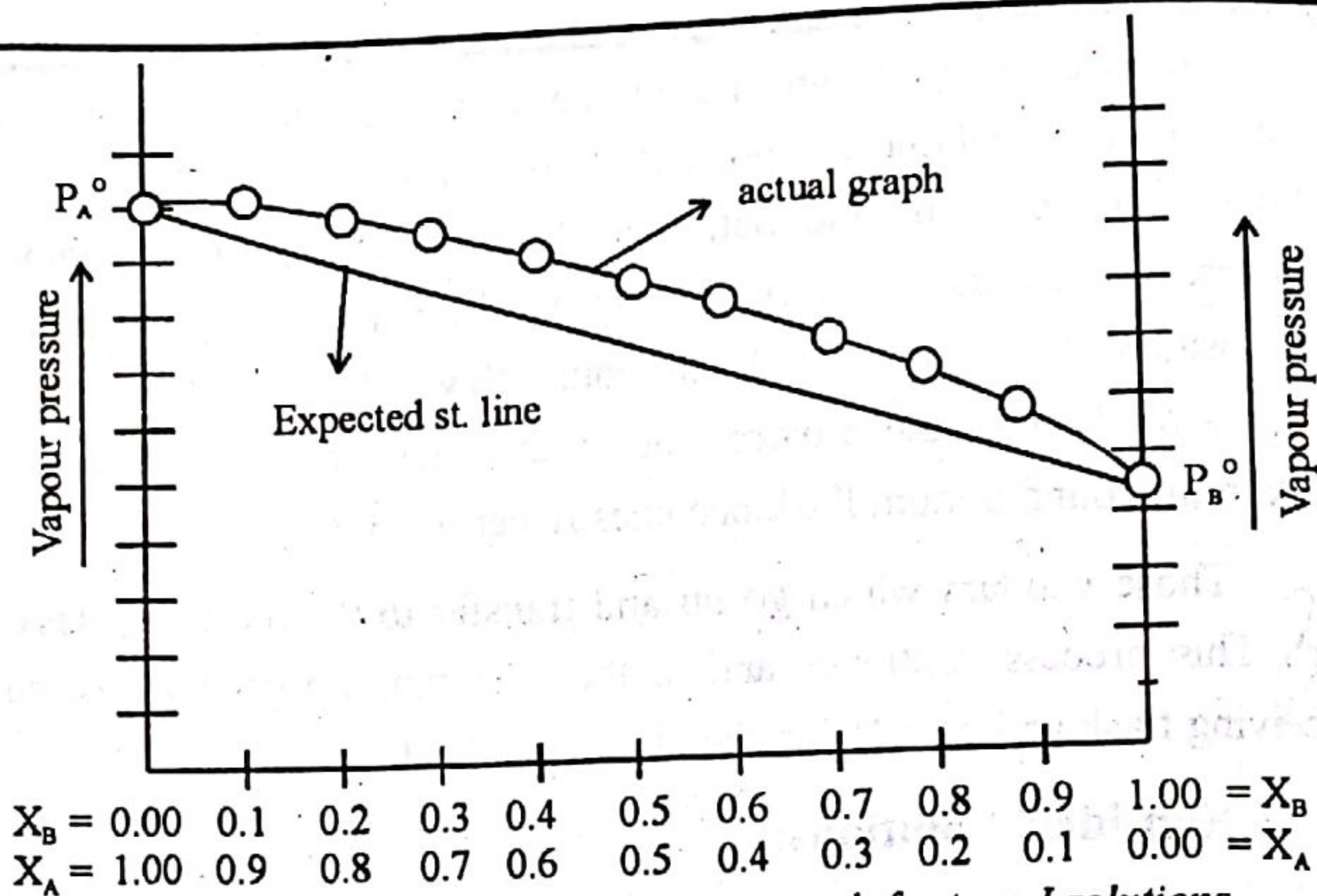
Fig. (6) Vapour pressure-composition graph for type-I solutions.

Some other examples in this reference are:

(i) CH$_3$OH + H$_2$O   (ii) C$_6$H$_6$ + C$_6$H$_5$CH$_3$

(iii) C$_6$H$_6$ + CCl$_4$ (iv) C$_6$H$_{12}$ + CCl$_4$

Such pairs of liquids create the forces of repulsion to some extent, as compared to pure components. This makes the vapour pressure greater than expectations.

TYPE-II:

Those pairs of liquids, which show a maximum point in the total vapour pressure curve, are said to show positive deviation from Raoult's law. Following graph (7) makes the idea clear.

Examples:

(i) C$_6$H$_6$ + C$_6$H$_{12}$ (ii) C$_6$H$_6$ + C$_2$H$_5$OH   (iii) C$_2$H$_5$OH + CHCl$_3$

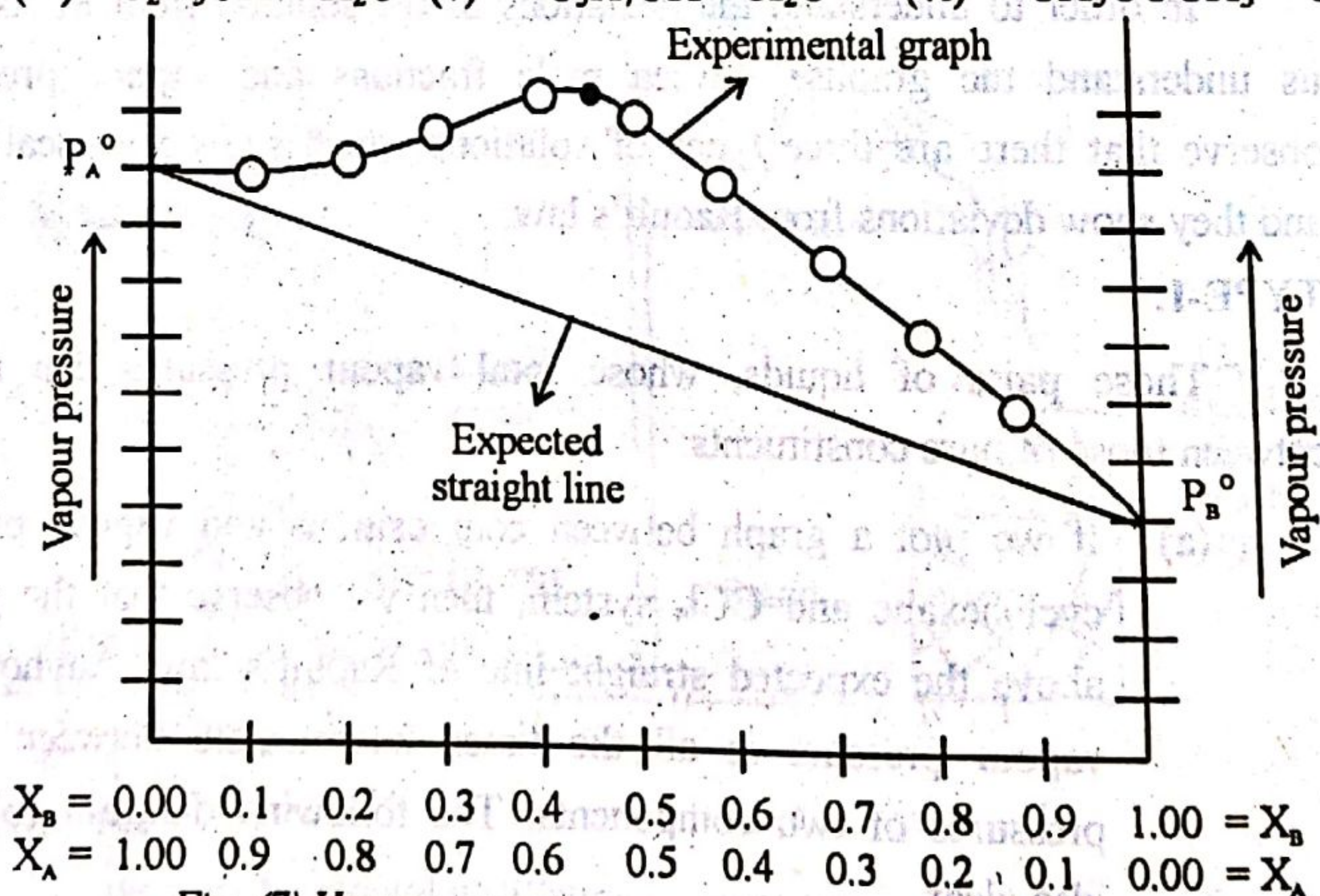(iv) C$_2$H$_5$OH + H$_2$O   (v) C$_3$H$_7$OH + H$_2$O   (vi) CH$_3$COCH$_3$ + CS$_2$

Fig. (7) Vapour pressure composition graph for solutions
showing positive deviation from Raoult's law.

TYPE-III:

Certain pairs of liquids show a minimum point in the total vapour pressure curve. They show the forces of attractions among the molecules of pure components. Following diagram (8) makes the idea clear.

Examples:

(i) $CH_3COCH_3 + CHCl_3$

(ii) $H_2O + HNO_3$

(iii) $H_2O + HCOOH$

(iv) $H_2O + HCl$
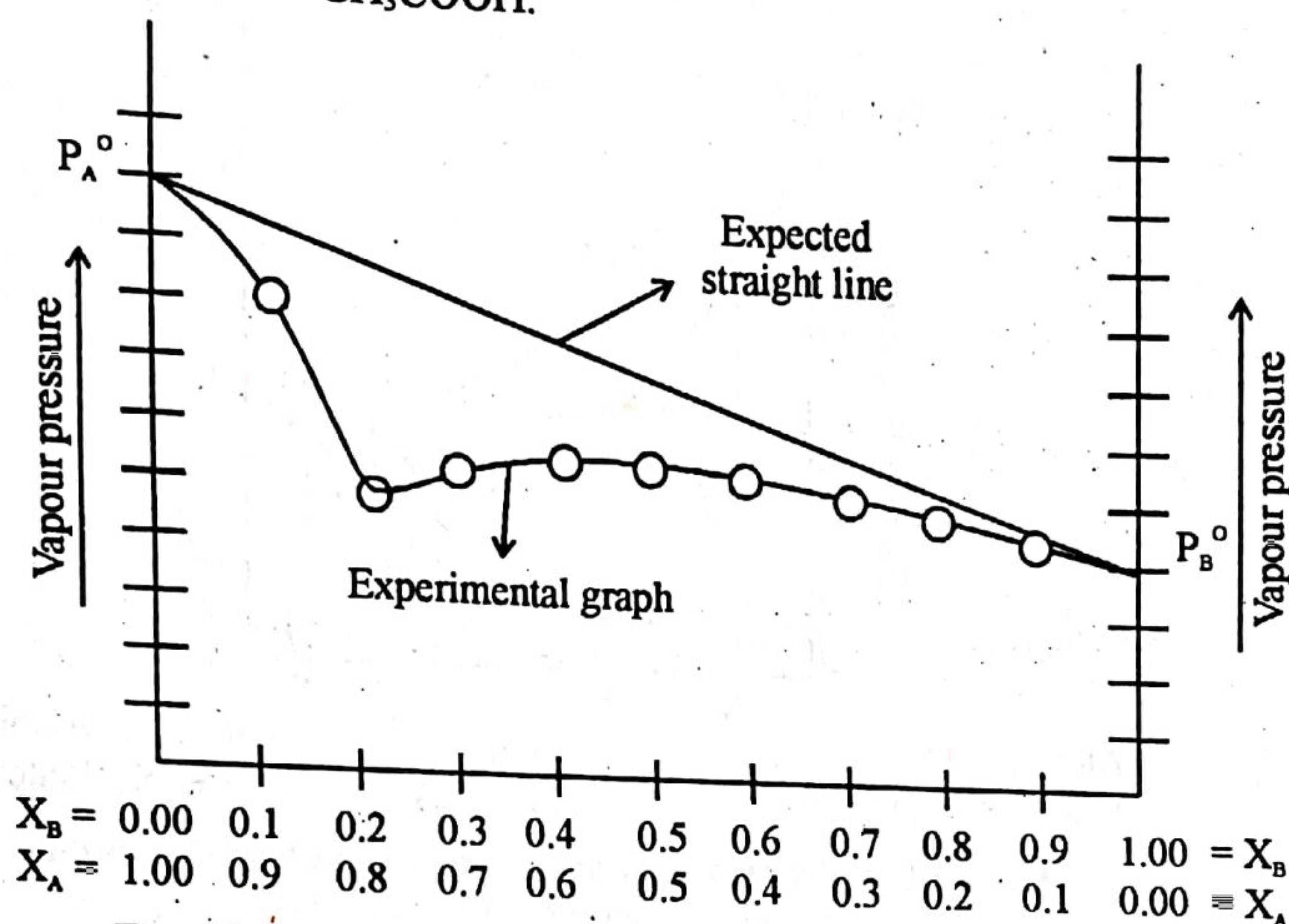
(v)   Pyridine $+ CH_3COOH$.

Fig. (8) Vapour pressure-composition graph for solutions showing negative deviation from Raoult's Law.

8.4.3 Fractional distillation of Non-ideal solutions:

We have discussed three types of non-ideal solutions. Let us, discuss the fractional distillation of these three types one by one.

TYPE-I:

Those pairs of liquids which do not show the maxima or minima in the vapour pressure composition curve, can be fractionally distilled and pure components can be separated from each other just like ideal solutions Fig. (6). *Such mixtures of liquids which make the ideal or non-ideal solutions and can be separated by fractional distillation are called zerotropic mixtures.*

TYPE-II:

In this type, we have discussed those pairs of liquids, which show the maximum point in the vapour pressure composition curve. They are said to show positive deviation from Raoult's law. They make an azeotropic mixture corresponding to the maximum point which can not be separated Fig. (7). The reason is that such a composition attains a common boiling point. The composition of the liquid and vapour is same.

In order to understand it, we have to plot a graph between boiling points and the composition Fig. (9).

Let us take the example of water and ethanol. In the diagram, the component 'A' is alcohol having boiling point 78.5°C and the component 'B' is water having boiling point 100°C. This pair of liquids gives a minimum boiling azeotropic mixture at 78.1°C.

In the diagram, the point 'C' corresponds to minimum boiling mixture, which is called azeotropic mixture of alcohol and H_2O.

$$Alcohol = (X_A) = 0.0 \qquad\qquad 0.0 = (X_A)\ Alcohol$$
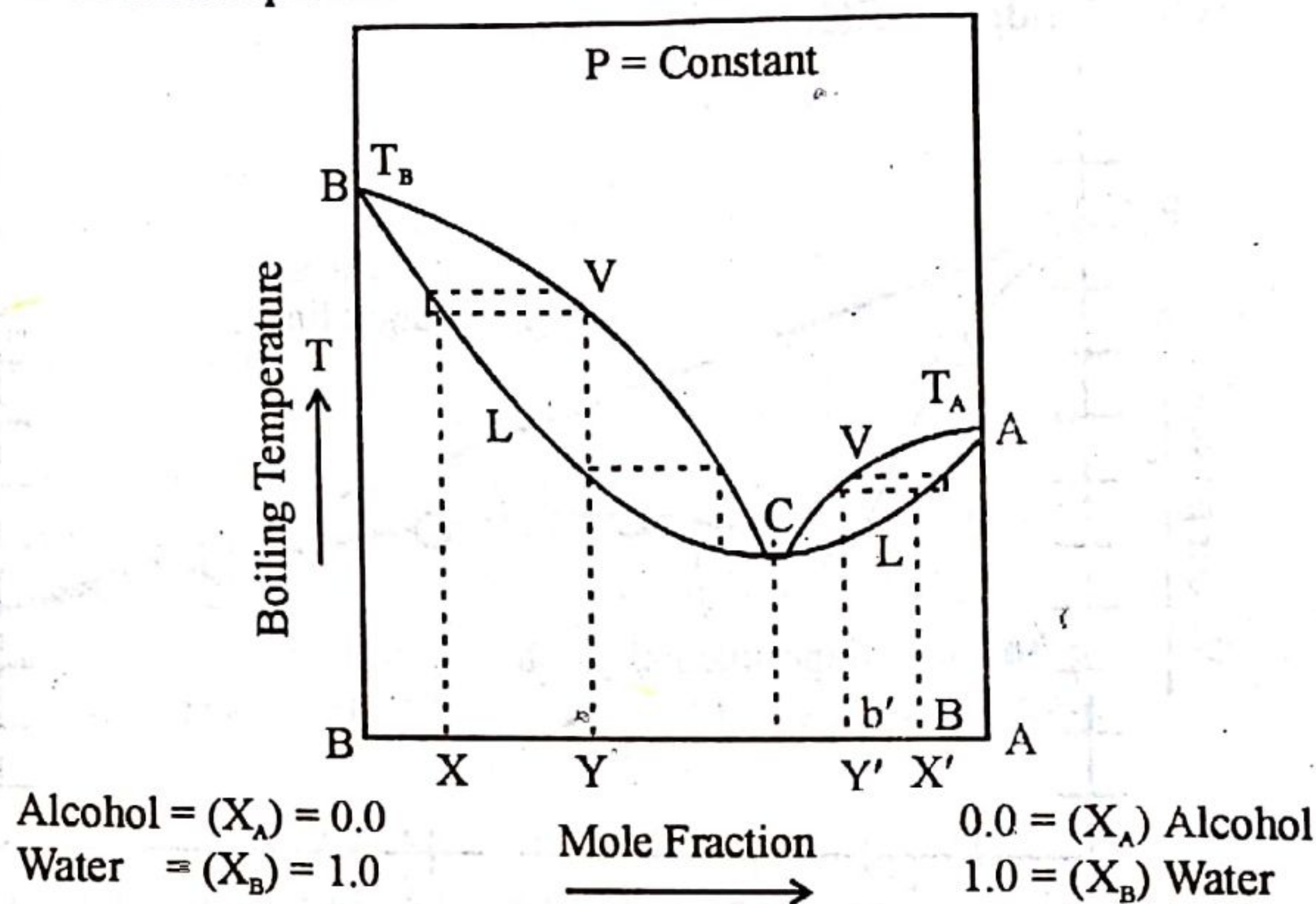$$Water = (X_B) = 1.0 \qquad\qquad 1.0 = (X_B)\ Water$$

Fig. (9) Distillation behaviour of solutions of type-II showing positive deviation from Raoult's Law.

If a solution of composition between 'B' and 'C' is distilled, then the vapours coming out will have different compositions than the liquid. Consider that we have a composition 'X' of H_2O and alcohol having greater % age of water than alcohol. Its composition will be 'Y' in the vapours state. In other words, the vapours will be richer in alcohol and the residue will be richer in water. It means that the composition of the residue will shift towards water and finally the pure water with boiling point 100°C will be obtained.

The liquid which is obtained on condensing the vapours with composition 'Y' is distilled. The vapours richer in alcohol will be obtained. If this condensation of vapours, and redistillation of liquid obtained is continued, then in the long run we get vapours of composition 'C'. These vapours on condensation will give a liquid which on redistillation will give the vapours which have the same composition as that of solution. At this stage, we can not do any separation by distillation. So, we can say that any mixture of composition between 'B' and 'C' on fractional distillation gives a residue of pure 'B' and final distillate of composition 'C'. Pure water can not be recovered.

Now, let us look at other side of this curve that is between 'A' and 'C'. Consider the liquid mixture having composition 'X''. When it is distilled, then the composition of vapours will be 'Y'' which will be richer in water as compared to

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the liquid state. So, the residue will be richer in alcohol. If the distillation is repeated, then residue of pure alcohol in a final distillate of composition 'C' will be obtained. This distillate is nothing but a constant boiling mixture 'C'. Pure alcohol can not be recovered.

All those mixtures of solutions, which show positive derivation from Raoult's law show a minimum boiling point azeotropic mixture. The boiling point of this mixture is lower than any other mixture of 'A' and 'B'.

TYPE-III

Those pairs of liquids which show the minimum point in the vapour pressure composition curve, show the maximum point, when the graph is plotted between boiling points and composition Fig. (10).
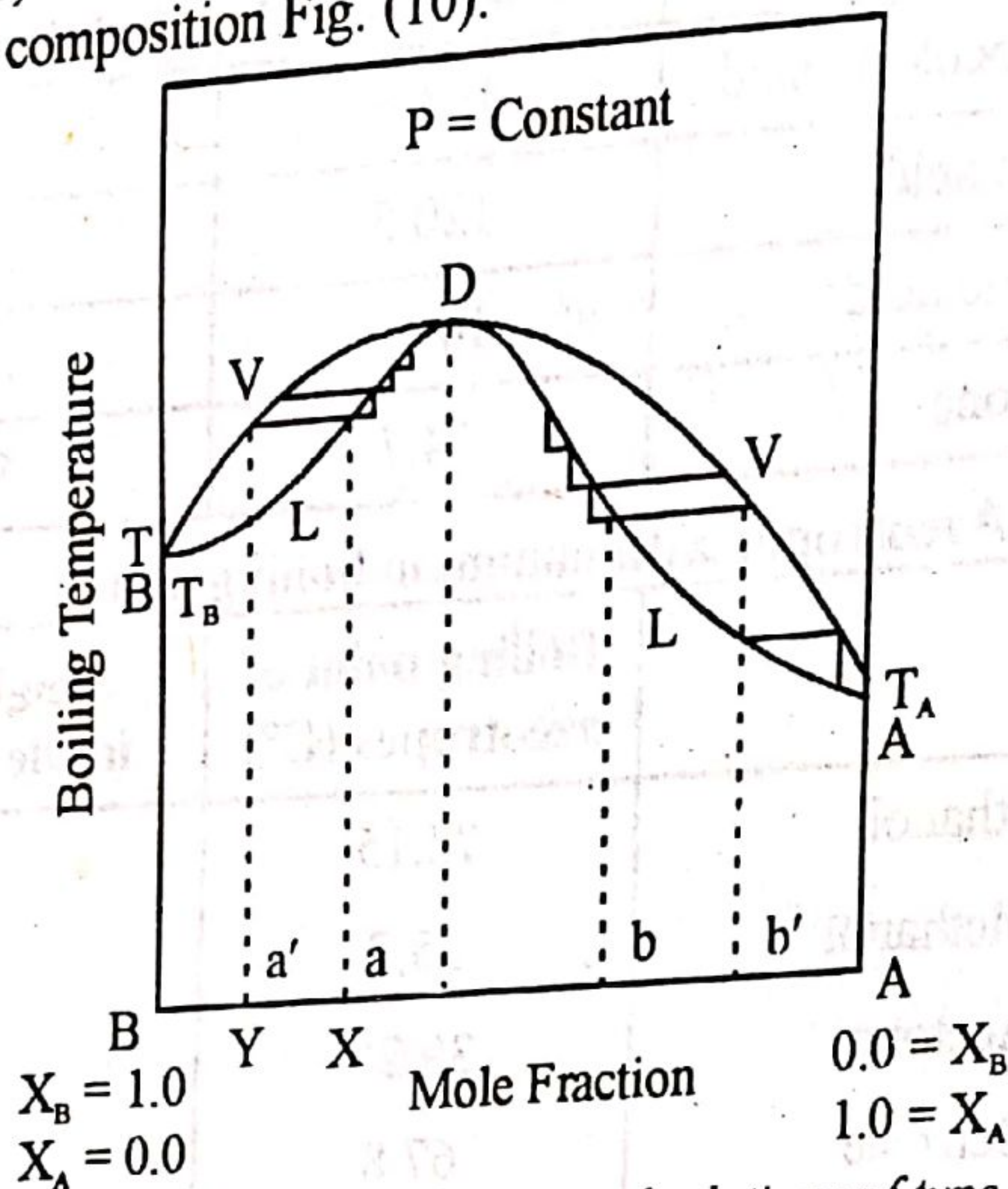

Fig. (10) Distillation behaviour of solutions of type-III, showing negative deviation from Raoult's Law.

According to the diagram, the solutions having compositions between 'B' and 'D', will be distilled as follows.

Take into the account the composition 'X' in the liquid state. The composition of the vapour is 'Y'. The vapours are richer in component 'B' and the residue will contain more of 'A'. It means that the composition of the residue will shift towards 'D'. When distillation is repeated again and again, a residue of solution of composition 'D' is obtained. The composition of vapours will shift towards 'B' and finally pure 'B' is obtained.

If means that the fractional distillation of this type of mixture solution gives pure component 'B' and a constant boiling mixture of composition 'D'.

If we look at the other part of the curve, then we can say that the fractional distillation of solution having composition between 'A' and 'D' will give pure component 'B' and the residue will have composition corresponding to 'D'.

8.4.4 Some important azeotropic mixtures:

The idea of the azeotropic mixture has been explained in above articles. These mixtures of liquids may be consisted of two components or more than two

components. They have definite compositions and boil at a constant temperature and distill over completely at the same temperature without any change in composition.

Although, they boil at constant temperature, they can not be regarded as pure compounds. Keep it in mind that the boiling point as well as the composition of an azeotrope changes with pressure.

Some important azeotropes are mentioned in the following tables (1) and (2).

Table (1) Azeotropes with maximum boiling points

A	B	Boiling point of azeotropes (°C)	Weight % of A in the azeotrope
Water	Hydrochloric acid	108.5	79.76
Water	Nitric acid	120.5	68.00
Pyridine	Formic acid	149.0	82.00
Chloroform	Acetone	64.7	80.00

Table (2) Azeotropes with minimum boiling points

A	B	Boiling point of azeotropes (C°)	Weight % of A in the azeotrope
Water	Ethanol	78.15	4.4
Carbontetra-chloride	Methanol	55.7	79.4
Carbon disulphide	Acetone	39.25	67.0
Ethanol	Benzene	67.8	32.2
Pyridine	Water	92.6	57.0
Carbon disulphide	Ethyl acetate	46.1	97.0

8.5.0 COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS

The properties of the solutions which depend upon the number of particles of the solute are called colligative properties. These are the properties of solutions and not of the pure substances.

There are four colligative properties:

(1) Lowering of vapour pressure

(2) Elevation of boiling point (ebullioscopy)

(3) Depression of freezing point (cryoscopy)

(4) Osmotic pressure.

Actually, all the colligative properties are developed due to the lowering of vapour pressure. All these properties are obeyed, when the following conditions are satisfied:

(i) Solution is dilute

(ii) Solute is non-volatile

(iii) Solute is non-electrolyte

Now, let us discuss these properties one by one

8.5.1 Lowering in vapour pressure:

We have already mentioned different statements of Raoult's law. When a non-volatile, non-electrolyte solute is dissolved in volatile solvent, then according to Raoult's law, the relative lowering of vapour pressure is equal to mole fraction of the solute

$$\frac{\Delta P}{P^o} = X_2 \qquad \text{...... (1)}$$

ΔP = Lowering of vapour pressing

P^o = Vapour pressure of pure solvent

X_2 = Mole fraction of solute.

The mole fraction of solute depends upon the number of moles of solute (n_2) and the total number of moles of solution. The mole fraction of solvent is n_1.

$$X_2 = \frac{n_2}{n_1 + n_2} \qquad \text{...... (2)}$$

So, $$\frac{\Delta P}{P^o} = \frac{n_2}{n_1 + n_2} \qquad \text{...... (3)}$$

Number of moles of any substance is the ratio of mass of the substance to its molar mass.

Hence, $$n_1 = \frac{W_1}{M_1}$$

$$n_2 = \frac{W_2}{M_2}$$

W_1 and W_2 are masses of the solvent and solute respectively in the solution. M_1 and M_2, are their molar masses

$$\frac{\Delta P}{P^o} = \frac{W_2/M_2}{W_2/M_2 + W_1/M_1} \qquad \text{...... (4)}$$

Equation (4), can simplified by considering that the solution is very dilute and hence 'n_2' can be ignored in the denominator. So, $\frac{W_2}{M_2} \approx 0$.

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

$$\frac{\Delta P}{P^o} = \frac{W_2 \times M_1}{M_2 \times W_1} \qquad \text{...... (5)}$$

With the help of this equation (5), we can calculate molar mass 'M_2' of the solute which is non-volatile non-electrolyte.

8.5.2 Lowering of vapour pressure as a colligative property:

In order to have the understanding of this fact, let us consider three solutions having 6 gram of urea, 18 g of glucose and 34.2 g of sucrose in 1000 g of water in separate vessels. These solutes are non-voltile and non-electrolyte. From the give quantities it is clear that, all these three solutions are 0.1 molal each. In each solution, there are $\frac{1}{10}$ of Avogadro's number of particles of solutes. In other words, every solution has 6.02×10^{22} particles of solutes.

You will observe that, all the three solutions have same lowering of vapour pressure. Hence, we prove that lowering of vapour pressure is a colligative property. In other words lowering of vapour pressure (ΔP) is independing of the nature of solute and their masses, but depends upon the number of particles of solute.

8.5.3 Methods for the measurement of lowering of vapour pressure:

Broadly speaking, there are two methods in this reference:

    (i)   Static method

    (ii)   Dynamic method

(i)   Static Method:

This is, also called differential manometric method. It is consisted of differential manometer having a U-tube. This U-tube should contain a liquid of low volatility and having low density. There are two bulbs A and B in this apparatus. One of the bulbs is filled with a pure solvent, white the other has a solution. The apparatus is put in a constant temperature bath.
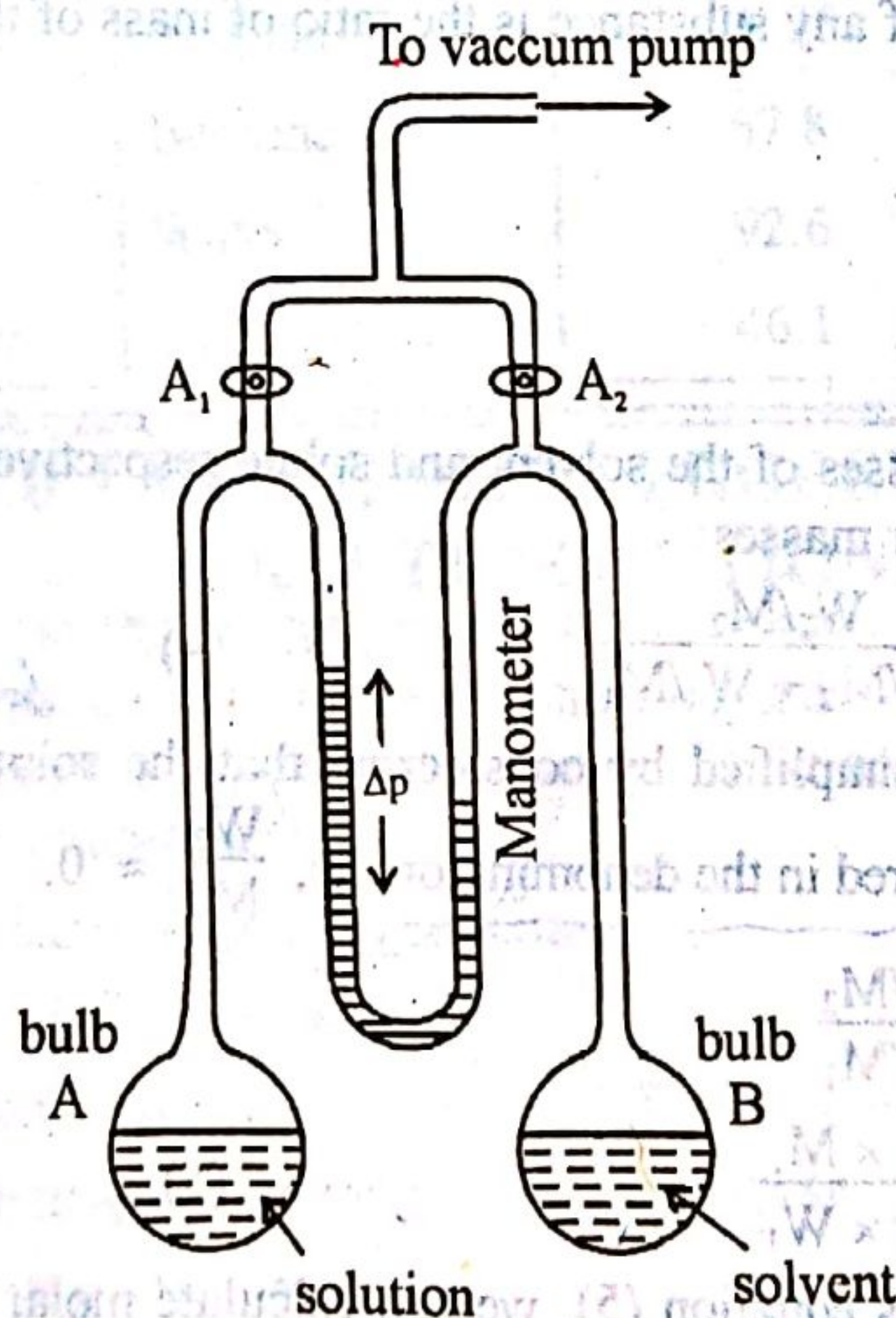

Fig. (11) *Differential manometer for vapour pressure measurement.*

The apparatus can be evacuated by the opening the taps A_1 and A_2, the difference in the level of the liquid in the two limbs of manometer is noted. It is the value of ΔP. Fig. (11).

(ii)   **Walker and Ostwald's Method:**

In this method, we have two types of bulbs, containing the solution having vapour pressure 'P' and the pure solvent having vapour pressure 'P°' Fig. (12). Dry air is successively passed through the solutions of nonvolatile solute and then through the pure solvent. After that, U-tubes are arranged which contain anhydrous $CaCl_2$ for absorbing the vapours of solvent which is generally water.

If the sets of the bulbs are weighed accurately before passing air, then we can determine the loss of the vapours from the bulbs containing the solution. The loss in the mass of the solution 'W_1', is proportional to 'P'.

$$W_1 \propto P$$

When this air is passes over the solvent bulbs, then it takes up the vapours of the solvent, till it is saturated upto P°. The additional amount of vapours taken up is proportional to the difference (P° – P). So,

So, $W_2 \propto P° - P$

or $P° - P \propto W_2$ ...... (1)

Hence, $P + (P° - P) \propto W_1 + W_2$

          $P° \propto W_1 + W_2$ ...... (2)

Now divide equation (1) with (2)

$$\frac{P° - P}{P°} = \frac{W_2}{W_1 + W_2}$$

$$\frac{\Delta P}{P°} = \frac{\text{Loss in the weight of solvent bulbs}}{\text{Total loss in the weight of solution and solvent}}$$

From the value of $\dfrac{\Delta P}{P°}$, we can calculate M_2 of solute
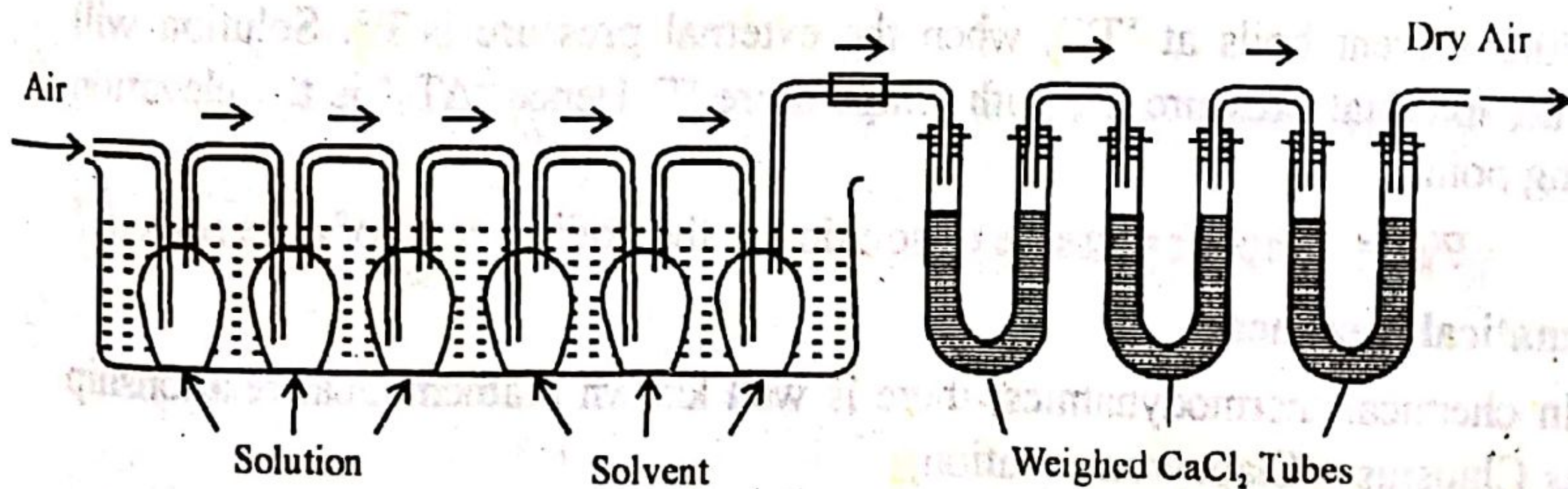

Fig. (12) *Walker's and Ostwold's method for measuring the lowering of vapour pressure.*

8.6.0 ELEVATION IN BOILING POITNS (Ebullioscopy)

As we have mentioned earlier, that the vapour pressures of solution containing non-volatile solutes are always lower than those of pure solvents at a constant temperature. It means that the vapour pressure of solution will never become equal to pure solvent at any temperature.

The elevation of the boiling point of solution depends upon the solvent and concentration of solution. It is independent of the nature of the solute for dilute solutions.

8.6.1 Graphical representation:

The elevation of the boiling point can be understood by plotting a graph between temperature and vapour pressure. The graphs of the solvent and the solution are as shown in the following diagram (13). Since, the vapour pressures of the solutions are always lower than the vapour pressures of pure solvent at all temperatures, so the graph 'CD' for the solution is lower than the graph 'AB' for the solvent.
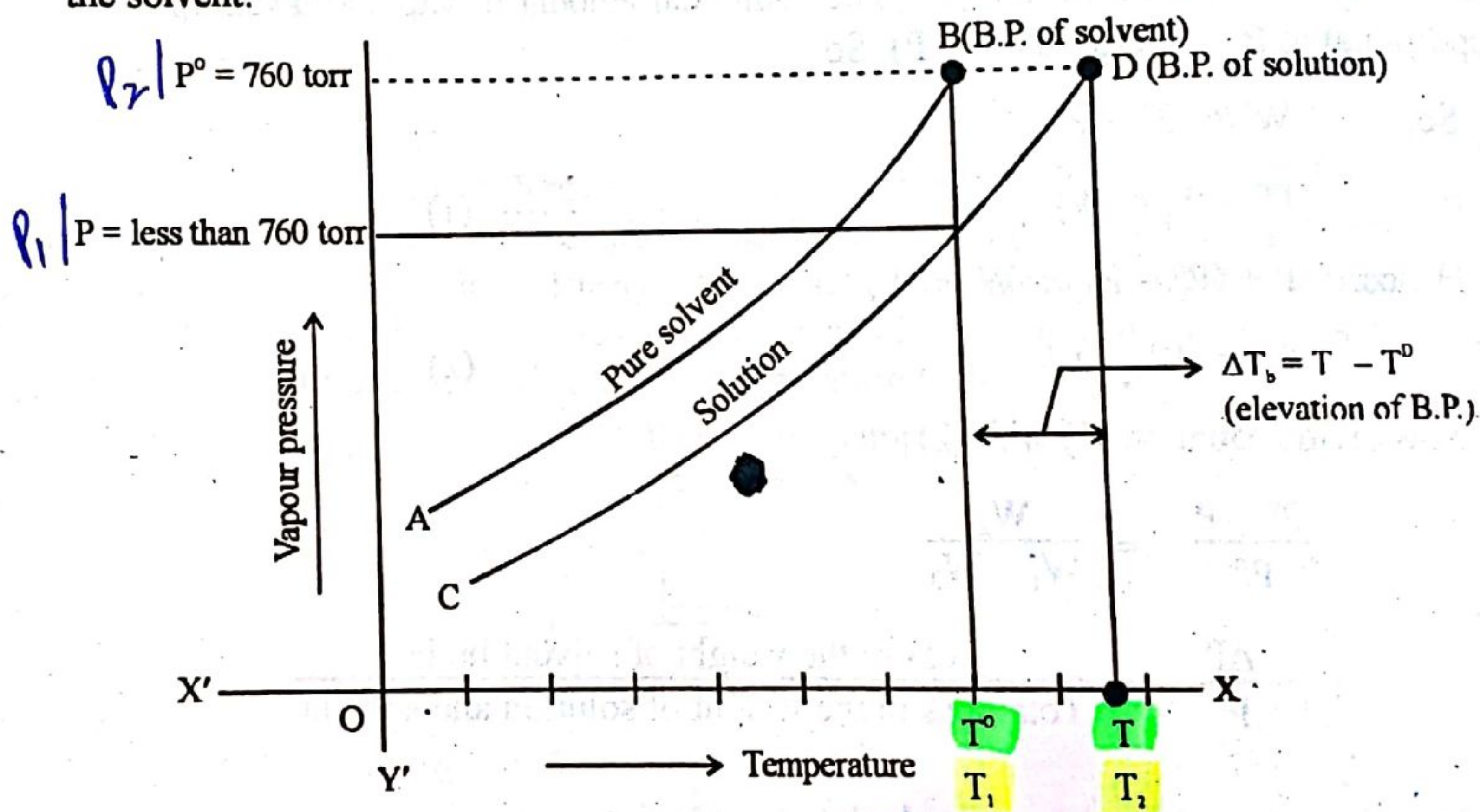
Fig. (13) Graphical representation of elevation of boiling point.

Pure solvent boils at 'T°', when the external pressure is P°. Solution will boil at the external pressure 'P', with temperature 'T' Hence 'ΔT_b' is the elevation of boiling point.

P =   Vapour pressure of solution at the boiling point of pure solvent

Mathematical treatment:

In chemical thermodynamics, there is well known mathematical relationship know as Clausius – Clapeyron equation,

$$ln\frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad \text{...... (1)}$$

According to this equation, a liquid has a vapour pressure 'P₁' at temperature 'T₁' and vapour pressure 'P₂' at temperature 'T₂'. (Here 'ln' stands for natural log where base is e). If we apply this equation to the above graph, then we can say that,

$$ln \frac{P^o}{P} = \frac{\Delta H_v}{R} \left[\frac{T - T^o}{TT^o} \right] \qquad \text{......} \quad (2)$$

ΔH_v = Heat of vapourization of the solvent. If the solution is dilute, the 'ΔH_v' is molar heat of vaporization of pure solvent.

By rearranging the above equation, and putting $T - T^o = \Delta T_b$

$$- ln \frac{P}{P^o} = \frac{\Delta H_v}{R} \left[\frac{\Delta T_b}{TT^o} \right]$$

$\begin{cases} X_1 = \text{mole fraction of solvent} \\ X_2 = \text{mole fraction of solute} \end{cases}$

Since, the solution is dilute,

Hence, $T \approx T^o$

So, $TT^o \approx T^{o2}$

$$- ln \frac{P}{P^o} = \frac{\Delta H_v}{R} \left[\frac{\Delta T_b}{T^{o2}} \right] \qquad \text{......} \quad (3)$$

Now, let us substitute the vapour pressure 'P' and 'P°' by mole fraction of the solution. This can be done by applying the Raoult's law.

Since, $P = P^o X_1$ (according to Raoult's law)

So, $\frac{P}{P^o} = X_1$

As, $X_1 + X_2 = 1$

So, $X_1 = 1 - X_2$

Hence, $\frac{P}{P^o} = 1 - X_2$

Putting values of $\frac{P}{P^o}$ in equation (3) in terms of mole fraction of solute

$$- ln (1 - X_2) = \frac{\Delta H_v}{R} \left[\frac{\Delta T_b}{T^{o2}} \right] \qquad \text{......} \quad (4) \qquad \rightarrow \text{Enpomson Technique}$$

L.H.S. of equation (4), can be simplified by the expansion technique

$$ln (1 - X_2) = - X_2 + \frac{X_2^2}{2!} - \frac{X_2^3}{3!} \text{......}$$

Since, the solution is dilute, so the value of 'X₂', in the form of squares and cubes becomes very small and can be ignored.

$\rightarrow X_2 \approx$ very very small

Hence, $ln (1 - X_2) \approx - X_2 \qquad \text{......} \quad (5)$

Put equation (5) in equation (4)

$$- (- X_2) = \frac{\Delta H_v}{R} \left[\frac{\Delta T_b}{T^{o2}} \right]$$

$$X_2 = \frac{\Delta H_v}{R} \left[\frac{\Delta T_b}{T^{o2}} \right] \qquad \text{......} \quad (6)$$

This equation (6), can be rearranged

$$\Delta T_b = \frac{RT^{o2}}{\Delta H_v} \cdot X_2 \qquad \cdots\cdots (7)$$

This equation (7) gives us the elevation of the boiling point of the solution. Anyhow, we should know the boiling point of pure solvent 'T°', heat of vapourization of the solvent and mole fraction of the solute 'X_2'.

Since, $\frac{R(T^{o2})}{\Delta H_v}$ is a collection of constant quantities, so, we can say that 'ΔT_b' is proportional to 'X_2'.

Since, $\qquad X_2 = \frac{n_2}{n_1 + n_2}$ 	_Since $n_1 \ggg n_2$_

In case of dilute solution 'n_2' can be ignored in the denominator,

So, $\qquad X_2 = \frac{n_2}{n_1}$

If we think that 'n_1' is the number of moles of solvent for 1000 grams of solvents, then 'n_2' will be molality of solution (m). Under such circumstances,

$$\therefore \qquad X_2 = \frac{m}{n_1}$$

Putting this value of 'X_2' in the above equation	_Kb = Ebullioscopic Constant_

$$\Delta T_b = \left[\frac{RT^{o2}}{\Delta H_v n_1}\right] m \qquad \cdots\cdots (8)$$

Molality? = gm mole/1000 g

We have taken 'n_1' inside the brackets because it is the number of moles of 1000 grams of solvent and all other parameters within the brackets are also related with the nature of solvent.

All the quantities in the brackets give another constant called K_b

$$K_b = \frac{RT^{o2}}{\Delta H_v n_1} \qquad \cdots\cdots (9)$$

$\therefore$ K_b is called molal boiling point constant or ebullioscopic constant. K_b is the elevation of boiling point when one mole of solute is dissolved in 1000 grams of solvent.

Hence $\qquad \Delta T_b = K_b \cdot m \qquad \cdots\cdots (10)$

$$\Delta T_b \propto m$$

It means that elevation of boiling point is directly proportional to the molality of solution.

We should be able to draw the following conclusions from equation (10).

(i) Elevation of boiling point is directly proportional to the molality of the solution.

(ii) The value of the K_b is independent of the nature and concentration of solution.

(iii) The observed and calculated value of K_b should agree with each other.

8.6.2 Calculation of molecular weights from elevation of boiling points:

If we put the value of molality in equation (10) from the basic definition of molality, i.e.

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

$$m = \frac{W_2}{M_2} \times \frac{1}{W_1 / 1000}$$

$$m = \frac{1000\, W_2}{M_2 . W_1} \qquad \cdots\cdots (11)$$

Substituting equation (11) in (10)

$$\Delta T_b = K_b \left(\frac{1000\, W_2}{W_1 \times M_2} \right)$$

or

$$M_2 = \frac{K_b}{\Delta T_b} \left(\frac{1000\, W_2}{W_1} \right) \qquad \cdots\cdots (12)$$

The molar mass of non-volatile non-electrolyte solute can be calculated from equation (12), we know the mass of solute W_2, mass of solvent 'W_1', elevation of B.P. ΔT_b, and 'K_b' value of the solvent.

8.6.3 Elevation of the boiling point as a colligative property:

In the above derived equation, we know that,

$$\Delta T_b = K_b . m$$

$$\Delta T_b \propto m$$

So, the elevation of boiling point depends upon the molality of solution and not upon the nature of the solute. Table (3)

Table (3) Molal boiling point elevation constant (K_b)

Solvent	B. P(C°)	Molal B.P. constant K_b . (C°/molal)
Aceitc acid	118.5	3.07
Acetone	56.00	1.71
Aniline	184.4	3.22
Benzene	80.15	2.53
Carbon disulphide	46.3	2.34
Carbon tetrachloride	76.50	5.03
Ethanol	78.26	1.22
Ether	34.42	2.02
Naphthalene	218.0	5.65
Phenol	181.8	3.56
Water	100.0	0.52

8.6.4 Relationship between elevation of boiling point and relative lowering of vapour pressure:

As we have already discussed, that the lowering of vapour pressure is responsible for the elevation of boiling point. Now let us try to have mathematical relationship between ΔT_b and $\dfrac{\Delta P}{P^o}$

$$\text{Since,} \quad \Delta T_b = K_b \frac{1000 \; W_2}{W_1 \cdot M_2} \qquad \cdots \cdots (1)$$

$$n_2 = \frac{W_2}{M_2} \qquad \cdots \cdots (2)$$

$$n_1 = \frac{W_1}{M_1}$$

$$\text{So,} \quad W_1 = n_1 \times M_1 \qquad \cdots \cdots (3)$$

Let us substitute the value of $\dfrac{W_2}{M_2}$ from equation (2) and W_1 from equation (3) in equation (1)

$$\Delta T_b = K_b \cdot \frac{1000 \cdot n_2}{n_1 \cdot M_1}$$

ØY

$$\Delta T_b = K_b \cdot \frac{1000}{M_1} \times \frac{n_2}{n_1} \qquad \cdots \cdots (4)$$

According to Raoult's law,

$$\frac{\Delta P}{P^o} = \frac{n_2}{n_1} \quad \text{(for dilute solutions)} \qquad \cdots \cdots (5)$$

Now replace $\dfrac{n_2}{n_1}$ by $\dfrac{\Delta P}{P^o}$ in equation (4)

$$\text{Hence,} \quad \Delta T_b = K_b \cdot \frac{1000}{M_1} \times \frac{\Delta P}{P^o} \qquad \cdots \cdots (6)$$

According to this equation, greater the lowering of vapour pressure greater the elevation of boiling point ΔT_b.

EXAMPLE (3)

When 0.419 g of the solute of molar mass 252.4 g mol^{-1} is dissolved in 75 g of the solvent, the boiling point of the solution is found to be 80.256 °C. Find the molal elevation constant (K_b). The boiling point of pure solvent is 80.2°C.

SOLUTION:

Data:

$$\text{B.P. of solution} = 80.256 \; ^\circ C$$

$$\text{B.P. of solvent} = 80.20 ^\circ C$$

$$\text{So,} \quad \Delta T_b = 80.256 - 80.2 = 0.056 ^\circ C = 0.056 \; K$$

$$\text{Mass of the solute} \; (W_2) = 0.419 \; g$$

$$\text{Molar mass of the solute} \; (M_1) = 252.4 \; g$$

Formula:

The expression for molar mass is

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

$$\text{or} \quad K_b = \frac{M_2 \, W_1 \, \Delta T_b}{1000 \times W_2}$$

Substituting the values,

$$K_b = \frac{252.4 \text{ g mol}^{-1} \times 75 \text{ g} \times 0.056 \text{ K}}{1000 \text{ g} \times 0.419 \text{ g}}$$

$$\boxed{K_b = 2.53 \text{ K mol}^{-1}} \quad \text{Ans.}$$

EXAMPLE (4)

At what temperature a solution containing 5.60 g of glucose per 100 g of water will boil. The value of ΔH_V at 100°C for water is 40585 J mol^{-1}, R = 8.314 J K^{-1} mol^{-1}).

SOLUTION:

Data:

First of all we determine the K_b value of the solvent

$$\text{Molar heat of vaporization of water at 100°C } (\Delta H_v) = 40585 \text{ J}$$

$$\text{Heat of vaporization of water per gram} = \frac{40585}{18} = 2254.75 \text{ J g}^{-1}$$

$$T_0 = 100°C = 100 + 273 = 373 \text{ K}$$

Formula:

The expression for K_b is, as

$$K_b = \frac{RT^2}{\Delta H_V \times n_1}$$

where $n_1 = \dfrac{1000}{M_1}$

$$K_b = \frac{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times (373 \text{ K})^2}{\dfrac{1000 \text{ g}}{18} \times 2254.7 \text{ J g}^{-1}}$$

$$K_b = \frac{1156718.5}{2254700}$$

$$K_b = 0.513°\text{K mol}^{-1} = 0.513\text{C}° \text{ mol}^{-1}$$

From the value of K_b, determine the ΔT_b value

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

Since,

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

$K_b = 0.513°$ K mol^{-1}, $W_1 = 100$ g, $M_2 = 180$ g mol^{-1}, $W_2 = .5.6$ g

Putting the values

$$\Delta T_b = \frac{1000 \text{ g} \times 0.513 \text{ K mol}^{-1} \times 5.6 \text{ g}}{100 \text{ g} \times 180 \text{ g mol}^{-1}} = 0.016 \text{ K} = 0.016°\text{C}$$

B.P. of solution $= 100 \text{ C}° + 0.016 \text{ C}° = \boxed{100.016 \text{ C}°} \quad$ Ans.

8.6.5 Determination of elevation of boiling point:

Mostly, there are two methods which are employed for determining the boiling point elevation 'ΔT_b' of dilute solutions.

    (i)   The Landberger's method

    (ii)   Cottrell's method

(i)   The Landberger's method:

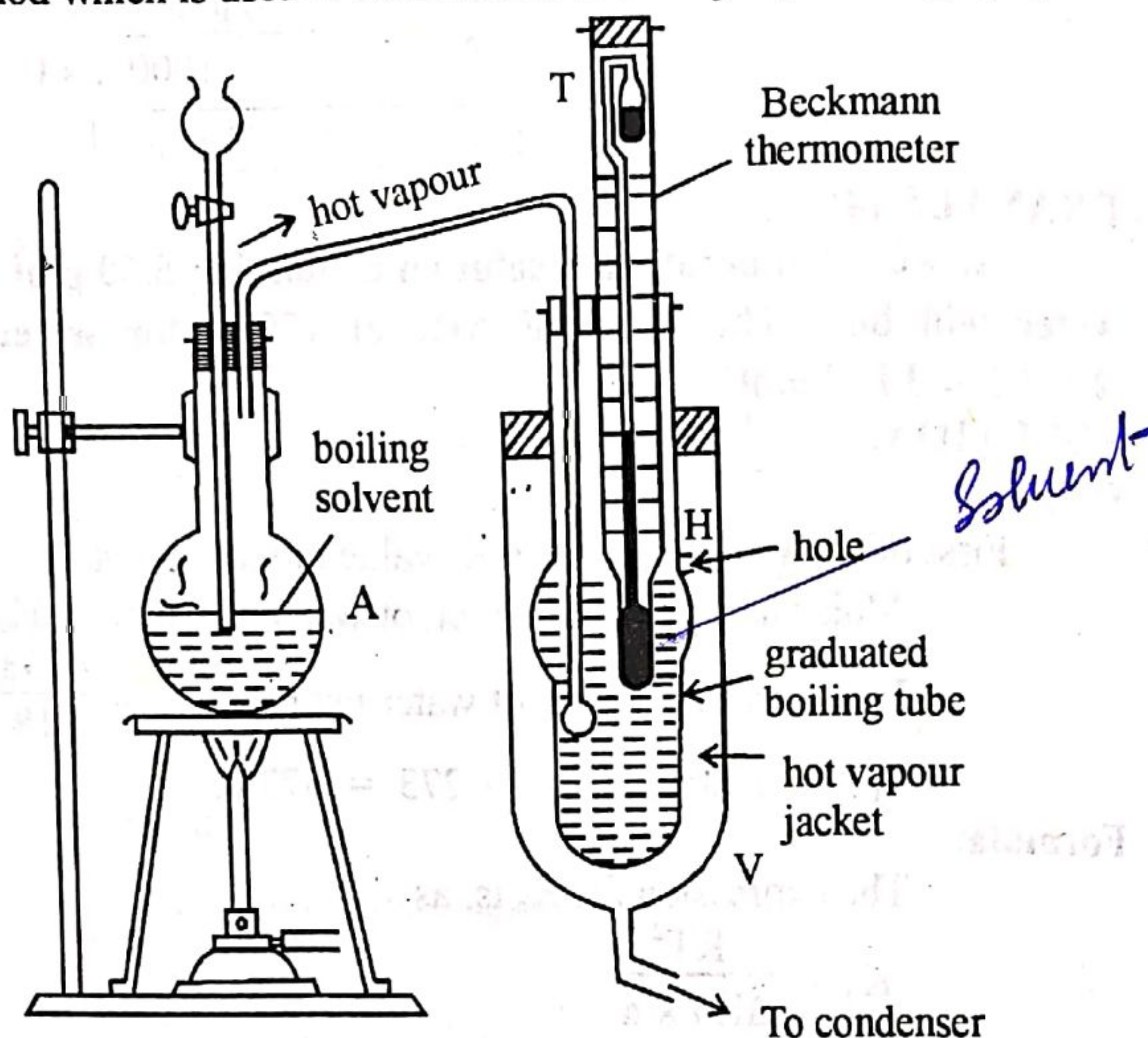The method which is used is consisted of four major parts. Fig. (14)

Fig. (14) Landberger's method for measurement of elevation of boiling point

    (i)   Boiling flask is used to boil the pure solvent and get its vapours.

    (ii)   An inner boiling tube whose middle portion is blown into a bulb and has a hole in the side.

    (iii) Beckmann thermometer which can read upto $\dfrac{1}{100}$th of a degree.

    (iv) Hot vapour jacket surrounding the inner glass tube.

Procedure:

Take 10 ml of the pure solvent in the inner boiling tube. The solvent is boiled in the flask and vapours are transferred to inner tube. The latent heat of condensation of the vapours raises the temperature in the inner tube upto its boiling point. The boiling point of the pure solvent is noted with the help of Beckmann's thermometer. Let this temperature be 'T^o'.

An accurately weighed quantity of solute is added in the inner tube and again the boiling point is noted as done previously. The volume of the solution at the stage of its boiling is measured. The density of this solution is determined later on. From the density and the volume, the mass of the solution in the inner tube is calculated.

From the mass of the solute, mass of the solvent and the elevation of the boiling point, we can calculate the molar mass of the solute.

(ii)   Cottrell's Method:

The apparatus is consisted of graduated tube 'A'. A liquid is placed in that and super heating is avoided because the vapours and the boiling liquid are sprayed on the bulbs of Beckmann's thermometer as shown in diagram (15). The total mass of the solvent remains the same as those of vapours on reaching the water condenser.

At the beginning, a weighed quantity of the solvent 'W₁', is taken in the boiling tube and it boiling point is noted. Then, it is cooled and a weighed quantity of the solute 'W₂' is added to that. Boiling point of solution is recorded and so the difference of boiling point is noted.

The mass of the solution is measured from the volume and density. In this way, the molar mass can be calculated.
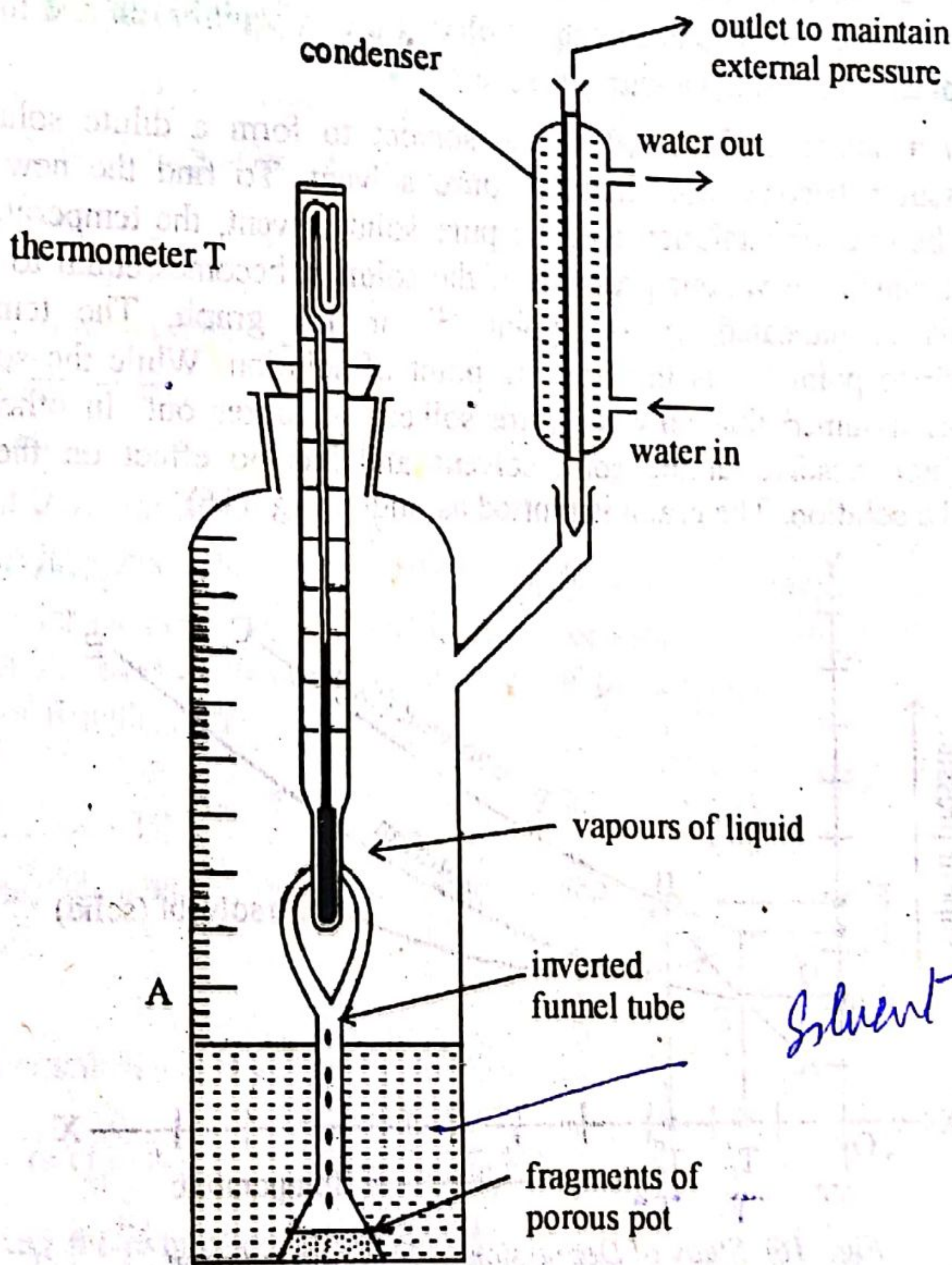

Fig. (15) Cottrell's boiling point apparatus for measurement of elevation of boiling point of a solution.

8.7.0 DEPRESSION IN FREEZING POINT (CRYOSCOPY)

Freezing point of the solution is the temperature at which the solution is in equilibrium with the solid solvent. Moreover, the freezing point of the solution is always less than that of its pure solvent. This is again due to the lowering of vapour pressure of solution.

8.7.1 Graphical representation:

In order to have a through understanding, let us plot a graph between temperature on x-axis and vapour pressure on y-axis. The curve 'BC' is for the liquid solvent and 'A' is the freezing point of pure solvent corresponding to the point 'B'. If the solvent is cooled further, then change of vapour pressure with temperature is given by the curve 'AB'. It means that the rate of change of vapour pressure with respect to temperature is very sharp for the solid solvent. This 'AB' curve is also called sublimation curve of the solvent. At the freezing point of the pure solvent "$T°$" the solid and the liquid phases are in equilibrium and the solvent in the both phases has same vapour pressure "$P°$".

When a solute is dissolved in the solvent to form a dilute solution, the vapour pressures become less than the pure solvent. To find the new state of equilibrium between the solution and the pure solid solvent, the temperature must be known at which the vapour pressure of the solution becomes equal to the solid solvent. This is indicated by the point 'F' in the graph. The temperature corresponding to point 'F' is the freezing point of solution. While the solution is freezing, it is assumed that only the pure solvent separates out. In other words, solute does not dissolve in the solid solvent and has no effect on the vapour pressure of the solution. The graph is plotted as under. Fig. (16)

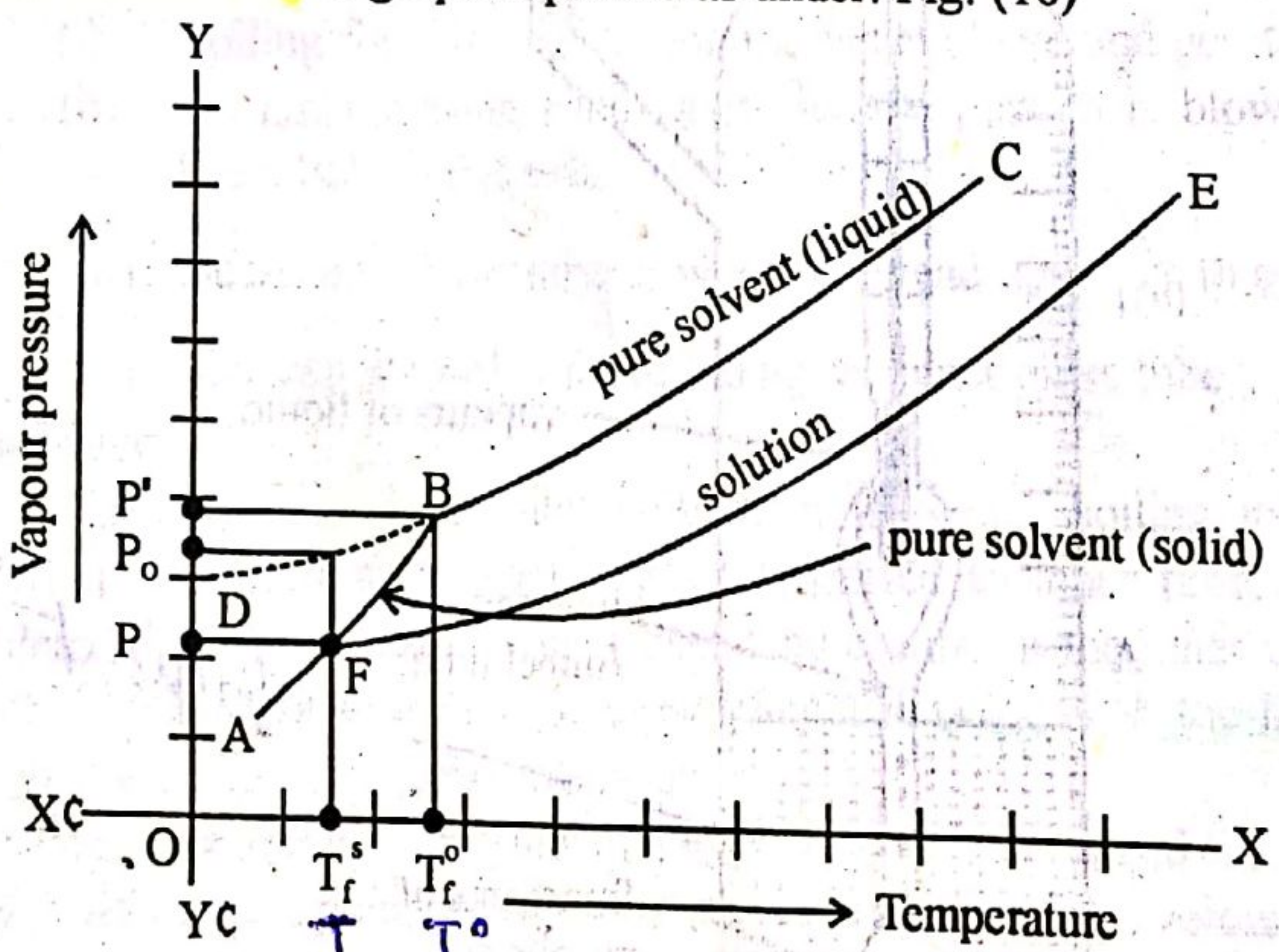*Handwritten margin notes: Sublimation curve; Solute does not dissolve; Solute separates out from freezing pure solvent*

Fig. (16) Study of Depression of F.P. of a solution.

The depression of freezing point is

$$\Delta T_f = T_f° - T_f^s$$

$$\Delta T_f = T° - T$$

Mathematical explanation:

We take the help of Clausius – Clapyeron equation, which relates the vapour pressures of the liquids with the temperatures of liquids.

Let P_s = V.P. of pure liquid and solid solvent at F.P. of pure solvent

P = V.P. of solid solvent and solution at temp. 'T_f^s' $\simeq T$

P^o = V.P. of pure super cooled liquid at 'T_f^s'

In order to apply Clausius – Clapeyron equation, we have the following proposal:

$$\ln \frac{P_s}{P^o} = \frac{\Delta H_v}{R} \left[\frac{T_f^o - T_f^s}{T_f^o T_f^s} \right] \qquad \ldots\ldots (1)$$

Here ΔH_v = Heat of vapourization of the pure solvent

The point 'F' and 'B' lie on the same sublimation curve. So they must be given by the following equation

$$\ln \frac{P_s}{P} = \frac{\Delta H_s}{R} \left[\frac{T_f^o - T_f^s}{T_f^o T_f^s} \right] \qquad \ldots\ldots (2)$$

Here, ΔH_s = Heat of sublimation of the solid solvent

Substract the equation (2), from (1), we get

$$\ln \frac{P}{P^o} = \frac{-\Delta H_f}{R} \left[\frac{T_f^o - T_f^s}{T_f^o T_f^s} \right] \qquad \ldots\ldots (3)$$

Keep it in mind that, during subtraction of equation (1) and (2), we have put

$$\Delta H_s - \Delta H_v = \Delta H_f$$

Equation (3), relates the vapour pressure of the solid solvent to the vapour pressure of the pure liquid solvent at temperature 'T_f^o'. Equation (3) also relates the vapour pressure of solution to that of pure liquid solvent at temperature 'T_f^o'.

Now let us apply the Raoult's law to equation (3) and convert the vapour pressure of the system to the mole factions of the components. According to first definition of Raoult's law

$$\frac{P}{P^o} = X_1$$

Since, $X_1 + X_2 = 1$, $\qquad X_1 = 1 - X_2$

So, $\qquad \frac{P}{P^o} = 1 - X_2$

The equation (3) is converted into,

$$\ln (1 - X_2) = -\frac{\Delta H_f}{R} \left[\frac{T_f^o - T_f^s}{T_f^o T_f^s} \right] \qquad \ldots\ldots (4)$$

During the expansion of the L.H.S.

$$\ln (1 - X_2) = -X_2 + \frac{X_2^2}{2!} - \frac{X_2^3}{3!} \ldots\ldots$$

Since, the solution is dilute, so the value of 'X_2' is very small. The square and cubes of 'X_2' become so small, that they become negligible.

$$\ln(1 - X_2) \approx -X_2$$

Equation (4) is converted into

$$-X_2 = -\frac{\Delta H_f}{R}\left[\frac{T_f^\circ - T_f^s}{T_f^\circ T_f^s}\right]$$

Since, $T_f^\circ - T_f^s = \Delta T_f$

~~Therefore~~ — $T_f^\circ T_f^s = T_f^{\circ 2}$ (solution is very dilute) $T \approx T^\circ$

Hence, $\qquad X_2 = \frac{\Delta H_f}{R} \cdot \frac{\Delta T_f}{T_f^{\circ 2}}$

Rearranging the above equation

$$\Delta T_f = \left[\frac{RT_f^{\circ 2}}{\Delta T_f}\right] X_2 \qquad \ldots\ldots (5)$$

Since $\qquad X_2 = \dfrac{n_2}{n_1 + n_2}$ and the solution is dilute, 'n_2' can be ignored in the denominator

$$X_2 = \frac{n_2}{n_1}$$

If the solution is taken in such a way that weight of the solvent is 1000 grams, then 'n_2' becomes the molality of solution. Equation (5) becomes,

$$\Delta T_f = \left[\frac{RT_f^{\circ 2}}{\Delta H_f \cdot n_1}\right] m \qquad \ldots\ldots (6)$$

All the factors within the brackets of equation (6) are constants and they depend upon the nature of the solvent.

Let us put this collection of constants as 'K_f', which is the molal freezing point constant of the solvent, or crysocopic constant

$$K_f = \frac{RT_f^{\circ 2}}{\Delta H_f \cdot n_1} \qquad \ldots\ldots (7)$$

Hence, equation (6) can be written as

$$\Delta T_f = K_f \times m \qquad \ldots\ldots (8)$$

Equation (8), is very useful in the sense that, we come to know that the depression of freezing point ΔT_f only depends upon the molality of solutions. So, ΔT_f is a colligative property.

8.7.2 Determination of molecular weight of solute:

Equation (8), can be modified by putting the value of molality 'm'

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

Hence equation (8) becomes,

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

Rearranging this equation

$$M_2 = \frac{K_f}{\Delta T_f} \times \left(\frac{1000\, W_2}{W_1} \right). \qquad \ldots\ldots (9)$$

If we know the 'K_f' value of the solvent table (4), depression of freezing point 'ΔT_f', weight of the solute 'W_2' and weight of the solvent 'W_1', then we can calculate the molar mass of non-volatile, non-electrolyte solute.

8.7.3 Important conclusions:

(i) The depression of freezing point 'ΔT_f' is directly proportional to the molality of solution and does not depend upon the nature of the solute.

(ii) . The value of 'K_f' is independent of the concentration and nature of solute.

(iii) The experimental and theoretical values of 'K_f' agree with each other.

Table (4) Molal freezing point constants or cryoscopic constants of some solvents.

Solvent	Normal F.P. (C°)	Molal F.P. (constants K_f (C°/molal)
Aceitc acid	16.6	3.90
Aniline	− 6.1	5.87
Benzene	5.48	5.12
Carbon disulphide	− 111.5	3.80
Carbon tetrachloride	− 22.96	−
Ethanol	− 114.5	−
Ether	− 116.3	1.79
Naphthalene	80.2	6.9
Phenol	40.9	7.27
Water	0.00	1.86

8.7.4 Relationship between depression in freezing point with lowering of vapour pressure:

Mathematical expression of 'ΔT_b' and 'ΔT_f' are exactly similar. So, the relationship of 'ΔT_f' with $\frac{\Delta P}{P^\circ}$ will be the same as we have derived previously for ΔT_b.

$$\Delta T_f = K_f \frac{1000\, \Delta P}{M_1\, P^\circ}$$

It means that, greater the lowering of vapour pressure 'ΔP', greater the lowering of freezing point.

EXAMPLE (5)

0.25 g of a solute are dissolved in 20 g of water and the F.P. of solution is − 0.42 °C. Calculate the molar mass of the solute. Molar heat of fusion of ice at 0°C is 6025 J. (R = 8.314 J K^{-1} mol^{-1}).

SOLUTION:

Data:

Molar heat of fusion of ice at 0°C (ΔH_f) = 6025 J mol^{-1}

Molar heat of fusion of ice g^{-1} = (ΔH_f) = $\dfrac{6025}{18}$ = 334.7 J g^{-1}

Formula:

Since

$$K_f = \frac{RT^2_0}{1000 \times \Delta H_f}$$

Putting these values in the equation

$$K_f = \frac{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times (273 \text{ K})^2}{1000 \text{ g} \times 334.7 \text{ J g}^{-1}} = 1.84 \text{ K mol}^{-1}$$

Formula:

The relation for molar mass of solute is

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

K_f = 1.84 K

ΔT_f = (− 0.42) = 0.42 K

W_1 = 20 g

W_2 = 0.25 g

Substituting there values, we get

$$M_2 = \frac{1.84 \text{ K mol}^{-1} \times 1000 \text{ g} \times 0.25 \text{ g}}{0.42 \text{ K} \times 20 \text{ g}}$$

$$\boxed{M_2 = 54.76 \text{ g mol}^{-1}} \quad \text{Ans.}$$

EXAMPLE (6)

Urea is dissolved in H_2O and B.P. of solution is 100.13°C. Calculate the freezing point of the same solution. (K_f = − 1.86°C, K_b = 0.52°C).

SOLUTION:

(i) First of all calculate the molality of the solution, and then determine the depression of F.P.

Data:

B.P. of solution = 100.13 °C

B.P. of solvent H_2O = 100 °C

ΔT_b = 100.130 − 100 = 0.13 °C

K_b = 0.520°C

We know that

Formula:

$$\Delta T_b = K_b \times \text{molality}$$

So, molality of the solution = $\dfrac{\Delta T_b}{K_b}$ = $\dfrac{0.130}{0.530}$ = 0.25

(ii) Calculating the depression in freezing point

Depression of freezing point (ΔT_f) = $K_f \times$ molality

$$\Delta T_f = 1.86 \ K \ m^{-1} \times 0.25 \ m$$
$$= 0.465 \ K$$

Depression in freezing point. (ΔT_f) = (Freezing point of solvent) −
(Freezing point of solution)
$$= 0 - 0.468 \ K$$

$$\boxed{\Delta T_f = -0.468 \ K = -0.468 \ °C}$$ Ans.

EXAMPLE (7)

A solution is containing 0.520 g of glucose $(C_6H_{12}O_6)$ dissolved in 80.2 g of water. Find the B.P. and F.P. of the solution. $K_f = 1.86 \ °C$, $K_b = 0.52°C$.

SOLUTION:

Data:

$$K_b = 0.52 \ K \ m^{-1} \text{ and } K_f = 1.86 \ K \ m^{-1}$$

Mass of glucose $= 0.52 \ g$

Molecular mass of glucose $(C_6H_{12}O_6) = 180 \ g \ mol^{-1}$

Mass of water $= 80.2 \ g = 0.0802 \ kg$

Formula:

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

$$m = \frac{0.52 \ g}{180 \ g \ ms^{-1}} \times \frac{1}{0.0802 \ Kg}$$

$$m = 0.036 \ \text{moles} \ Kg^{-1}$$

Formula:

(i) Calculation of boiling point of solution

So $\Delta T_b = K_b \times$ molality

$$\Delta T_b = 0.52 \ Km^{-1} \times 0.036 \ m$$
$$= 0.01873 \ K = 0.019 \ K$$

B.P. of solution = B.P. of pure solvent + ΔT_b = 373 K + 0.019 K

$$= \boxed{373.019 \ K} \quad \text{Ans.}$$

Formula:

(ii) Calculation of freezing point of solution

$$\Delta T_f = K_f \times \text{molality}$$
$$\Delta T_f = K_f \times m$$
$$= 1.86 \ Km^{-1} \times 0.036 \ m$$
$$= 0.067 \ K$$

∴ Freezing point $= (273 - 0.067) \ K$

$$= \boxed{272.932 \ K} \quad \text{Ans.}$$

8.7.5 Determination of depression of freezing point:

Mostly two methods are employed for determining the freezing point.

(i)   The Beckmann's method.

(ii)   The Rast method.

(i)   The Beckmann's Method:

The apparatus which is used for the determination of depression of freezing point, has three important parts.

(i)   The inner freezing point tube

(ii)   The outer tube

(iii) A glass vessel.

Following diagram makes the idea clear Fig. (17).

In the experiment, 15 – 20 grams of the solvent is taken in the inner freezing point tube. Since, freezing mixture is taken in the glass vessel it will cool the solvent through the air jacket, created due to the outer tube. The solvent in the tube is gently stirred and the fall of temperature is noted by Beckmann's thermometer. As the solvent starts solidifying the temperature starts rising and becomes steady after sometime. This temperature is noted, because it is the freezing point of pure solvent.
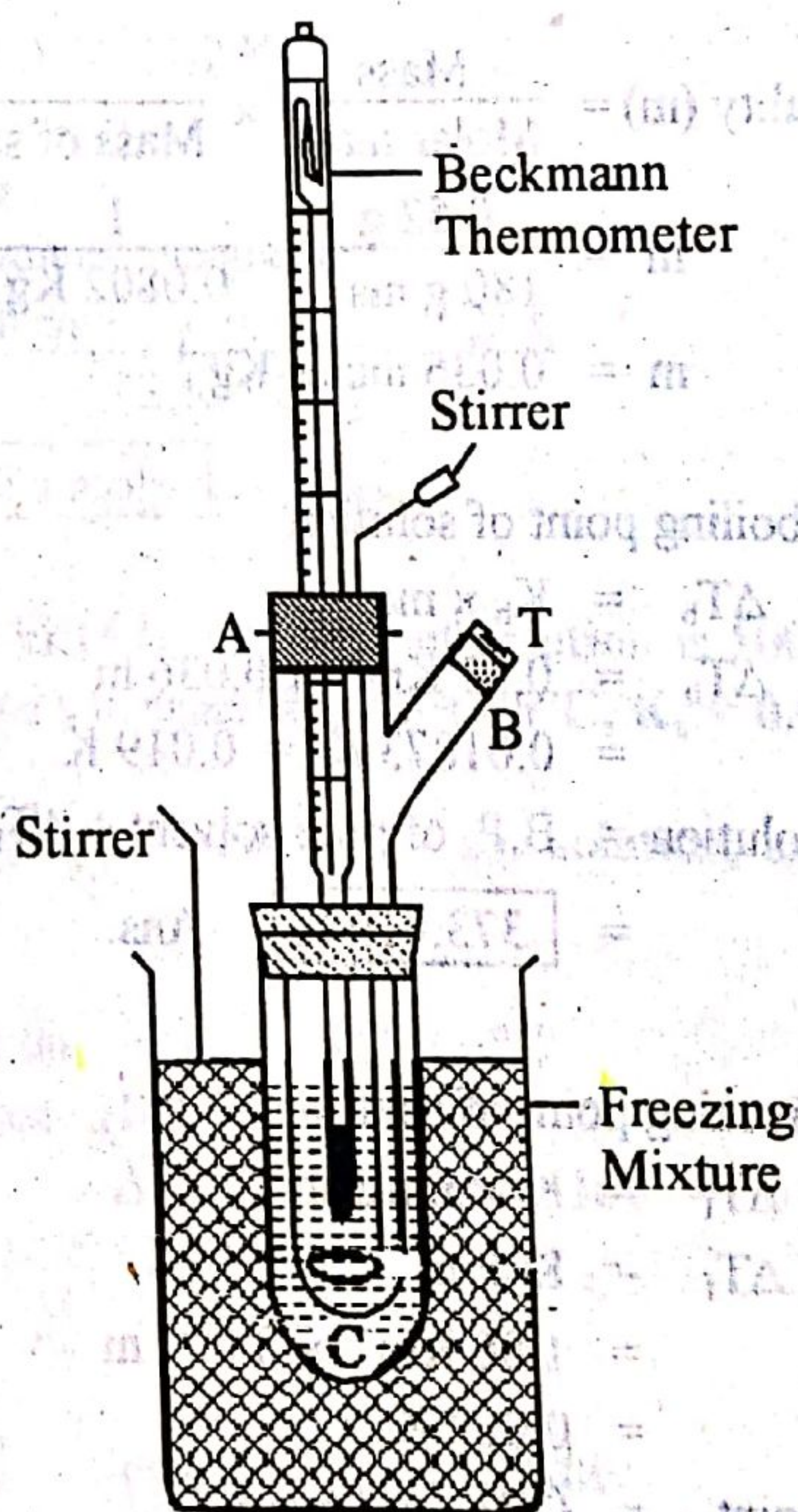

Fig. (17) Beckmann's apparatus for the determination of depression of freezing point.

Tube is taken out of the freezing mixture and the solid solvent is remelted and accurately weighed quantity of the solute as 0.1 – 0.2 grams is added through the side tube of the inner tube. This inner tube is again placed in the freezing mixture and the contents are gently stirred. The temperature of the solution slowly falls. When it becomes steady, then it is noted. The difference of these two temperatures is 'ΔT_f'. This experiment can be repeated by adding different quantities of the solutes. The depression of freezing point will change and the molar mass of the compound remains the same.

(ii)   The Rast camphor Method:

In this method, camphor is a used as a solvent. Hence, only those solutes can be employed which are soluble in camphor. Actually, the 'K_f' value of camphor is 37.7°C. It means that even very dilute solution of a solute in camphor will have reasonable depression of freezing point. In this way, ordinary thermometer can be used in place of Beckmann's thermometer. The method is the same, as we have discussed above.

Other suitable solvents in place of camphor:

(i)   Hexachloroethane.

(ii)   Tetrabromomethane.

Comparison of methods:

In Rast method, only those solutes can be employed which are soluble in camphor, so this method has limited scope when we keep in view the nature of the solutes. Anyhow, this method is superior to Bechmann's method, in the sense that

(i)   Ordinary thermometer can be used

(ii)   Method is very sensitive

(iii)   Very small quantity of the solute can do the work.

8.8.0 OSMOSIS

When a solution is separated from its solvents by a semipermeable membrane, then the solvent flows to the solution side through the membrane.

"This flow of the solvent from higher solvent concentration to lower solvent concentration is called osmosis".

8.8.1 What is semipermeable membrane:

A semipermeable membrane is a thin layer which permits the passage of only one type of molecules, generally the solvents.

Examples:

(i)   Parchment

(ii)   Fish bladder

(iii)   Lining of egg shell

(iv)   Cellophane

A semipermeable membrane acts as sieve in the study of osmosis.

8.8.2 Experimental study of osmosis:

Nollet was the person who did first experiment on osmosis in 1748. A simple arrangement is that a piece of parchment is tightly stretched across the belly of the thistle funnel as shown in the following diagram. Fig. (18)
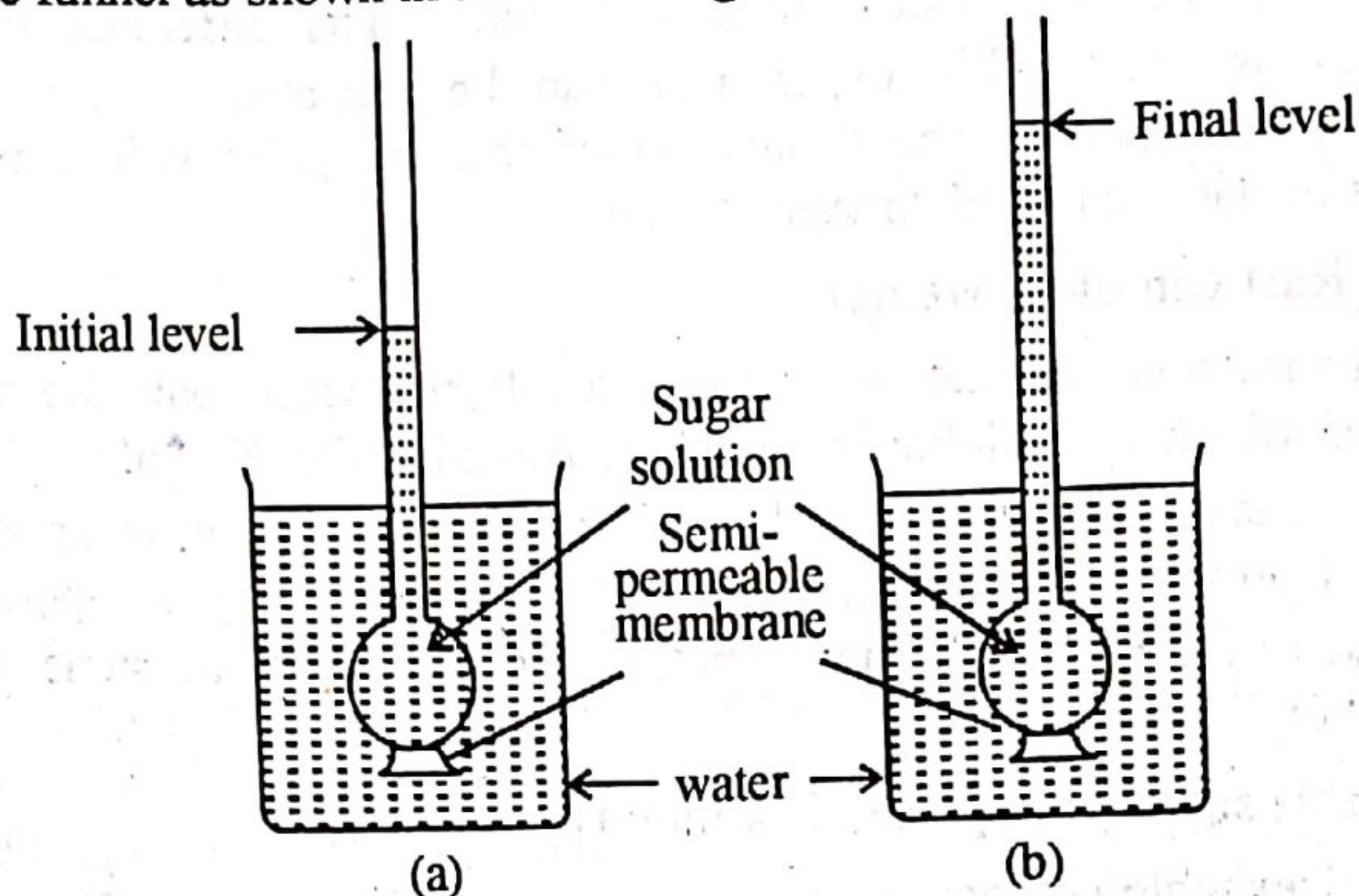

Fig. (18) Process of osmosis.

The funnel is filled in a concentrated solution of sugar and it is placed in a beaker of water. The level of the liquid in thistle funnel rises and then stops after attaining certain height.

8.8.3 Reason for the rise of liquid column:

When the semipermeable membrane is between the solution and the solvent, the solute molecules bombard the membrane and set up a pressure. Actually the molecules of the solvent flow on both sides, but the net bombardment of the solvent molecules from the pure solvent side is greater. In the process of osmosis the flow of solvent stops, when the hydraulic pressure on the other side of membrane is equal to osmotic pressure.

Definition:

"Osmotic pressure is the excess pressure which must be exerted on the solution side, in order to check the flow of the solvent molecules towards the solution side, when both are separated by semipermeable membrane."

8.8.4 Preparation of the semipermeable membrane:

The measurement of the osmotic pressure requires the use of suitable semi permeable membrane. Naturally occurring membranes such as animal and protein membranes are mechanically weak and are not perfectly semipermeable.

Some gelatinous inorganic substances such as $Ca_3(PO_4)_2$ and $Cu_2[Fe(CN)_6]$ are better membranes. Membrane is prepared on a porous pot. First of all porous pot is cleaned by washing with acid, alkali and finally with excess of water. Some air bubble entraped in the pores are removed by placing it in distilled water for a few hours. 2.5 % solution of $CuSO_4$, is filled in it, and then it is placed in a solution of 25 % $K_4[Fe(CN)_6]$ solution. The two solutions on the opposite side of the porous part permeate through the wall of the pot. Fig. (19)

A gelatinous precipitate of $Cu_2[Fe(CN)_6]$ is produced in the interior of the pot where the two solution meet. The reaction is as follows

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow 2K_2SO_4 + Cu_2[Fe(CN)_6]$$

When the reaction is complete then the pot is removed and it is carefully washed with water. This method is not so popular and it was disapproved by Morse and Fraser.

8.8.5 Electrodeposition of $Cu_2[Fe(CN)_6]$ membrane:

In this method, dilute $CuSO_4$ solution is filled in the porous pot and this pot is placed in $K_4[Fe(CN)_6]$ solution Fig. (19). A copper rod is suspended in the porous pot. A platinum wire is connected with a vessel outside. Copper rod acts as anode and platinum wire as cathode. Electric current is passed. Cu^{+2} ions and $[Fe(CN)_6]^{-4}$ more in opposite directions. They meet inside the pores of the porous pot and make $Cu_2[Fe(CN)_6]$. The pot is taken out and is placed in distilled water for a few days. This semipermeable membrane so formed is fairly strong and can tolerate a pressure of 270 atmospheres.
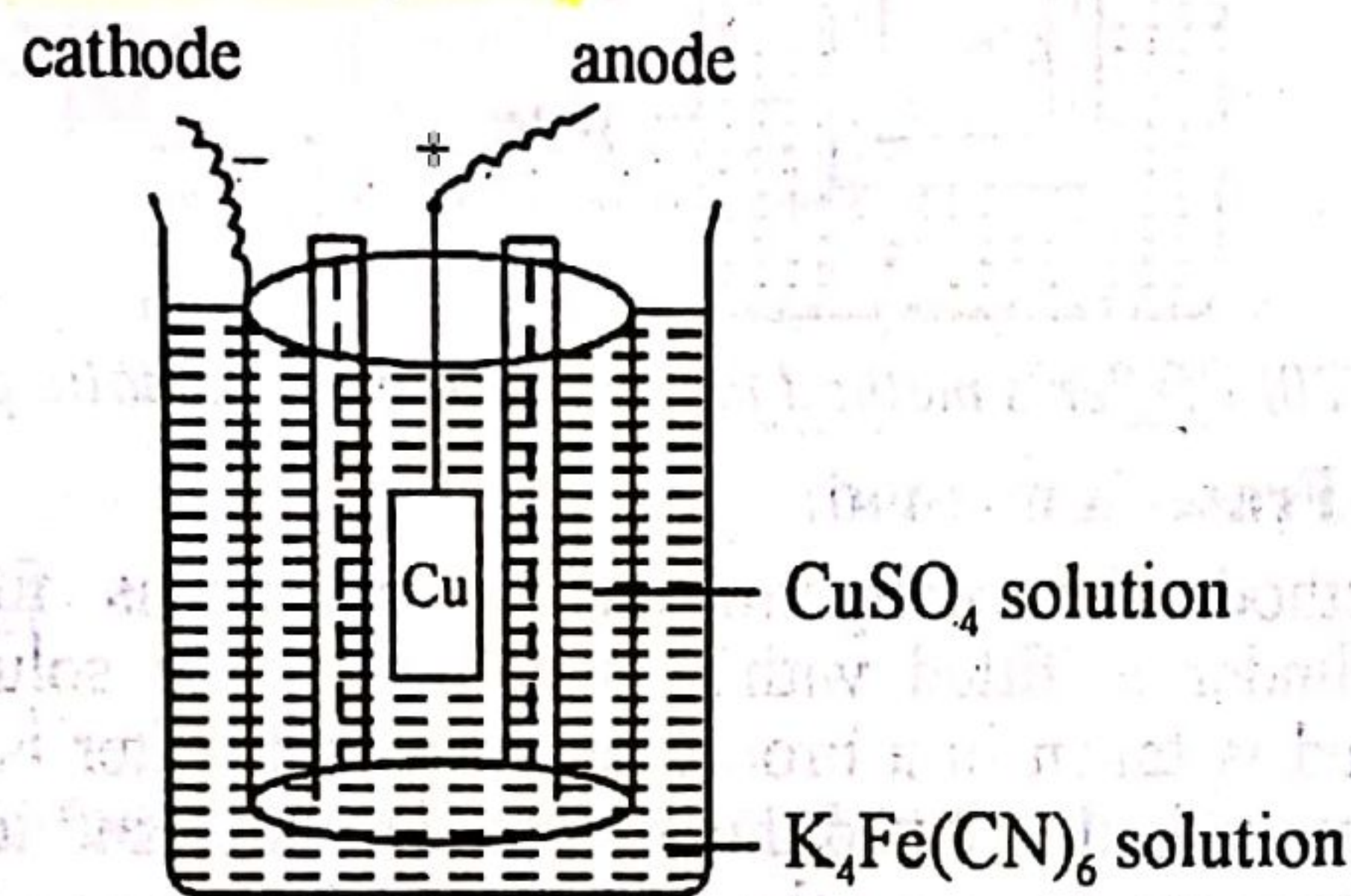

Fig. (19) Electrodeposition of copper ferrocyanide membrane.

8.8.6 Measurement of osmotic pressure:

There are three important methods in this respect:

(i)   Pfeffer's method

(ii)   Morse and Frazer's method

(iii)· Brekly and Hartley's method.

(i)   Pfeffer's method:

The arrangement is shown in the diagram (20). The semipermeable membrane of $Cu_2[Fe(CN)_6]$ is used. The solution whose osmotic pressure is required is placed in a glass tube which is connected to a manometer. The tube along with the semipermeable membrane is kept in water bath. Constant pressure is developed within a few days due to osmosis. The value of osmotic pressure can be read directly on the manometer.

Drawbacks of this method:

(i)   It is a time consuming experiment and takes many days to attain the equilibrium.

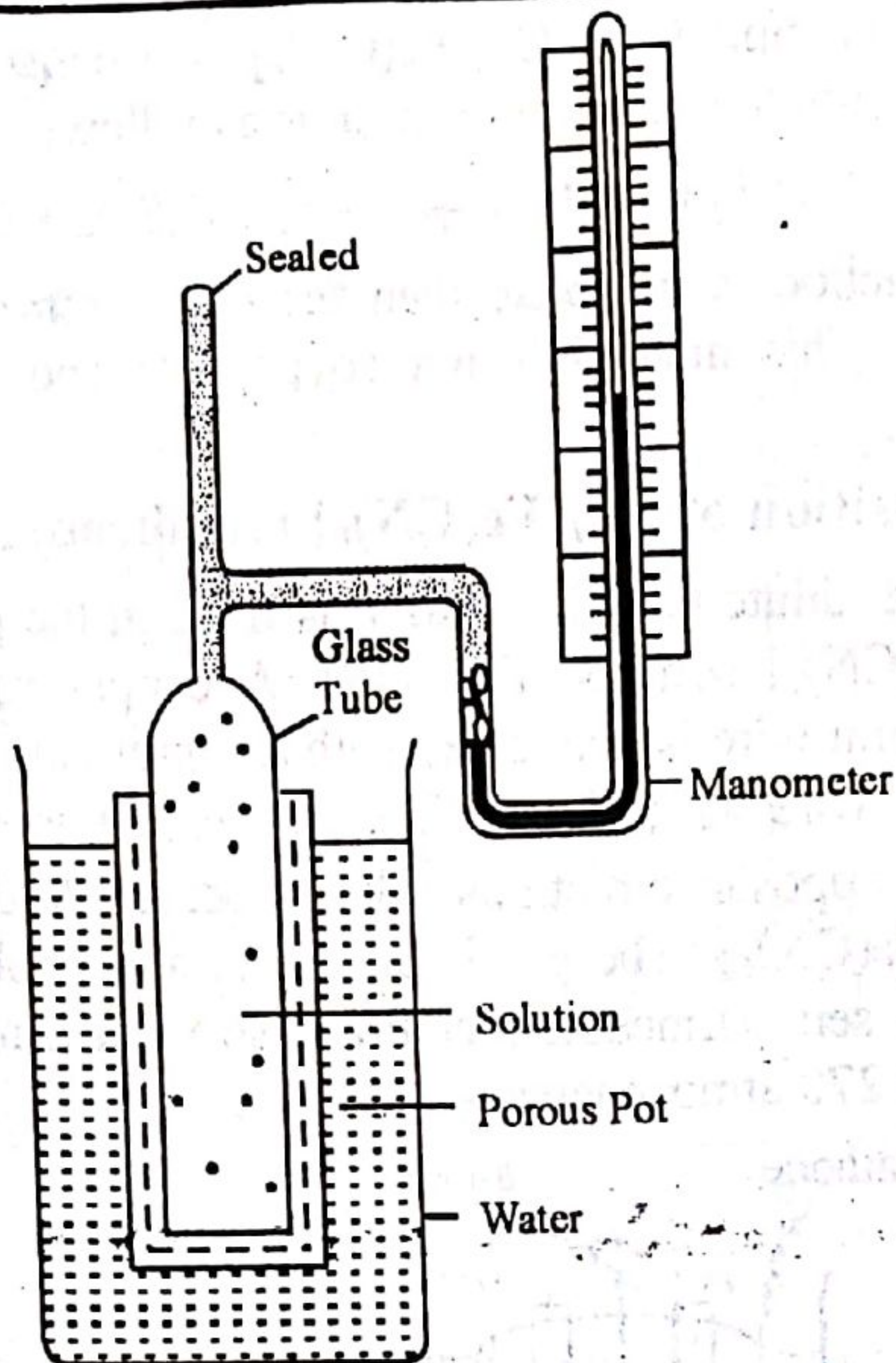(ii)   If high osmotic pressure is created, then the membrane may burst.

Fig. (20) Pfeffer's method for measuring the osmotic pressure.

(ii)   Morse and Frazer's method:

In this method, the semipermeable membrane is fitted with a bronze cylinder. This cylinder is fitted with a membrane. The solution whose osmotic pressure is required is taken in a bronze cylinder and water is taken in the porous pot. Constant pressure is developed due to flow of water and it can be registered in the manometer. One can measure the osmotic pressure upto 273 atmospheres by this method. Following diagram (21) makes the idea clear.
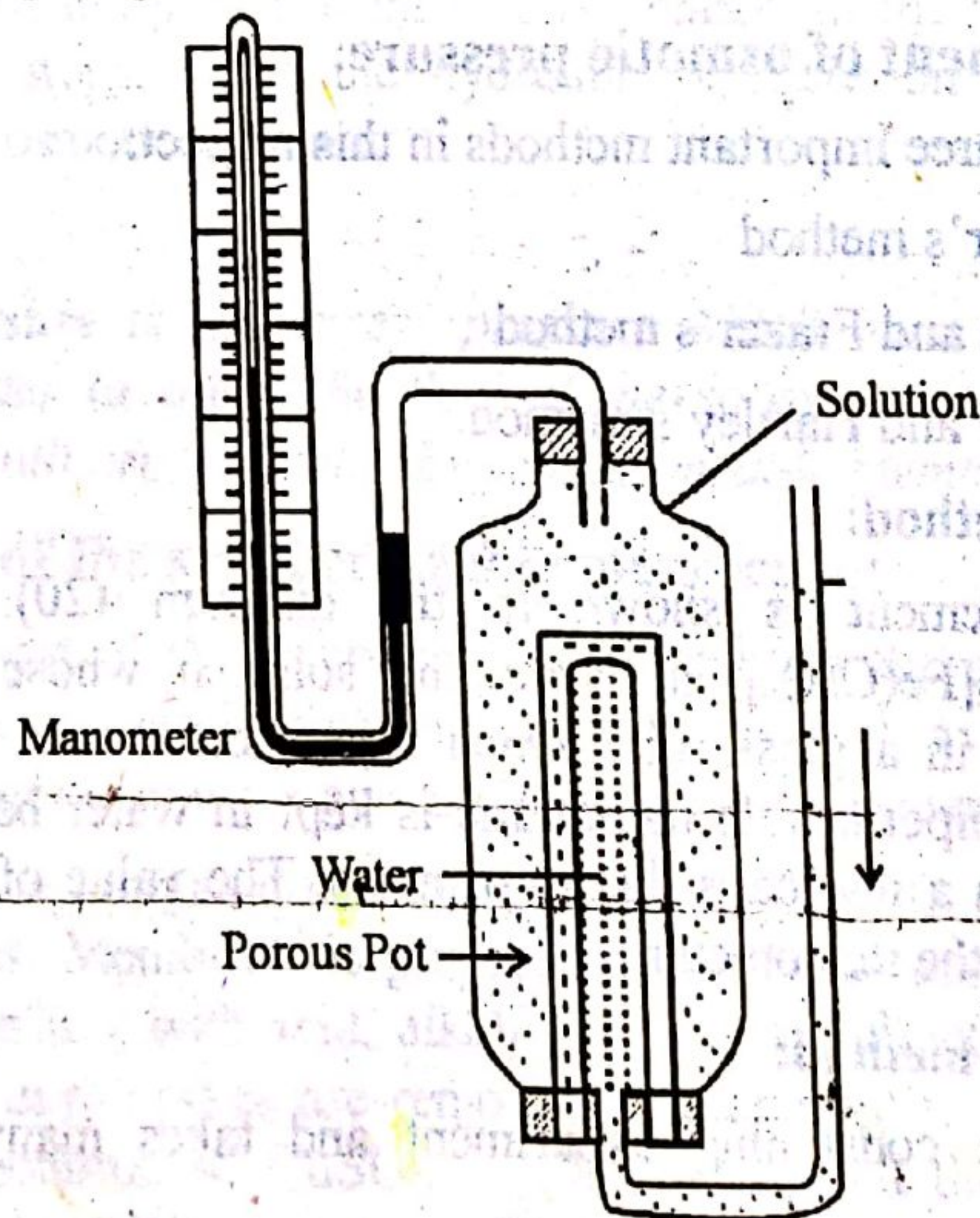

Fig. (21) Morse and Frazer's method for measuring osmotic pressure.

(iii) Berkley and Hartley's method:

This apparatus is consisted of porous pot at both the ends. $Cu_2[Fe(CN)_6]$ acts as a membrane. The porous pot is sealed into an outer bronze cylinder filled with a solution and water is taken in the porous pot.

Bronze cylinder is fitted with a piston. Weights can be placed on this piston to exert pressure on the solution. When water flows towards the solution, then the pressure is applied with the help of the piston, so that the water level in the tube becomes stationary. This external pressure is the osmotic pressure of the solution. Following diagram (22) shows the arrangement.
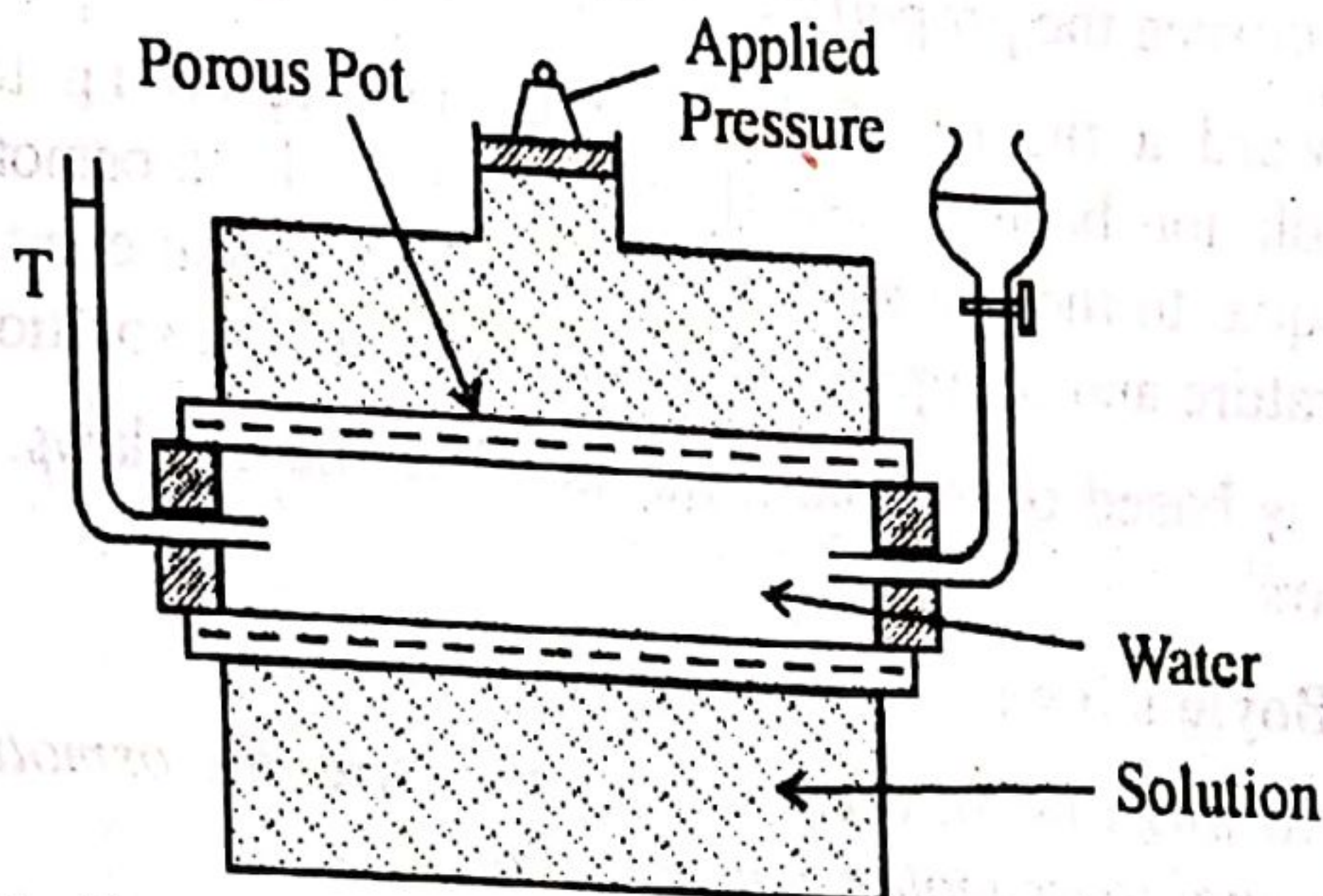

Fig. (22) Berkley and Hartley's Method for osmotic pressure measurement.

Advantages of Berkley's method:

(i) This is a very quick method.

(ii) During the determination of osmotic pressure, the concentration of solution does not change.

(iii) There is no danger for the bursting the membrane.

Values of osmotic pressures of sugar solution:

Following table shows the values of osmotic pressure of sucrose solution at 30°C (303 K).

Table (5) Osmotic pressures of sucrose solutions

Sucrose/kg of water	Osmotic pressure (atmosphere)
220 gm	15.48
370 gm	29.72
420 gm	74.94
1430 gm	148.46

8.8.7 Isotonic solutions:

Let us have two solutions of different concentrations in same the solvent. They are separated by semipermeable membrane. Then the solvent molecules flow from the solution of lower osmotic pressure towards the solution having higher osmotic pressure. This process will continue until both the solutions attain the same osmotic pressure. *"Such a pair of solutions which produce no flow of solvent molecules through semipermeable membrane are called isotonic solutions."*

Actually they have same osmotic pressures. For example, if we have 6 g of urea in 100 g of water on one hand and 18 g of glucose in 100 g of water on the other hand, then these two solutions will be isotonic.

8.8.8 Laws of osmotic pressure:

In order to understand the laws of osmotic pressure, we should look at the van't Hoff's equation of dilute solutions.

Vant Hoff studied the results of osmotic pressure measurement on aqueous solutions. He obtained good results by Pfeffer's method. He declared that there is strict parallelism between the properties of gases and dilute solutions.

He put forward a theory of dilute solutions. According to this theory, a substance in the solution behaves exactly like a gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert, if it were a gas at the same temperature and occupying the same volume as a solution.

This theory is based on simple laws, just like the gas laws. These laws are discussed, as follows.

(1) Vant Hoff-Boyle's law:

"According to this law, at a certain temperature, the osmotic pressure of a solution is proportional to its molar concentration."

$$\pi \propto C \qquad \text{(at const. temperature)}$$

$$\pi = K.C. \qquad \text{(at const. temperature)}$$

$$\frac{\pi}{C} = \acute{K} \qquad \text{(at const. temperature)}$$

Since, concentration of the solution is inversely proportional to volume.

$$C = \frac{1}{V}$$

Hence, $\pi V = K$

This is just like a Boyle's law for gases according to which PV = constant, at a constant temperature.

(2) Pressure – Temperature law:

"According to this law the osmotic pressure of a solution is proportional to absolute temperature at a given concentration."

$$\pi \propto T \qquad \text{(when concentration is const.)}$$

$$\pi = KT \qquad \text{(when concentration is const.)}$$

$$\frac{\pi}{T} = K \qquad \text{(when concentration is const.)}$$

This is just like the pressure temperature law for gases

$$\boxed{\frac{P}{T} = K}$$

(3) **Van't Hoff-Avogadro's law:**

"According to this law, the equimolal solutions of different solutes have the same osmotic pressure provided that the solute donot undergo association or dissociation."

This law can also be stated as follows. "Under identical conditions of temperature, equal volumes of two solutions exerting equal osmotic pressures will contain equal number of molecules of the solute".

$$\pi \propto n$$

(4) **General equation for solutions:**

In the above mentioned three laws, we have been given the idea that

$$\pi \propto \frac{1}{V}$$

$$\pi \propto T$$

$$\pi \propto n$$

If all these three parameter V, T and n vary simultaneously, then

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

$$\pi = (\text{constant}) \frac{nT}{V}$$

$$\pi V = (\text{constant}) \, nT$$

The value of the constant determined by various experiments is general gas constant 'R'.

So $\qquad \pi V = nRT$

This equation is identical to ideal gas equation

$$PV = nRT$$

It is found that the dilute solutions behave just like ideal gases.

Van't Hoff's law and Raoult's law:

Vant Hoff's law of osmotic pressure can be deduced from Raoult's law of lowering of vapour pressure. Raoult's law is applicable to dilute solutions, when the solutes are non-volatile, non-electrolyte. So Van't Hoff's law in its present form is also applicable to dilute solutions of non-volatile, non-electrolyte substances.

Limitations of Vant Hoff's law:

This law holds only, if a solution of non-electrolyte is not greater than 0.1 molality. The % age of the deviation increases, when the concentration of the solution increases. This law also fails in the case of solutions of electrolytes which give higher values of osmotic pressures than calculated by osmotic pressure law.

8.8.9 Osmotic pressure as a colligative property:

We have derived the general equation for solutions as,

$$\pi V = nRT$$

$$\pi = \frac{n}{V} \cdot RT$$

$$\pi = C \cdot RT$$

At constant temperature,

$$\pi \propto C$$

It means that <mark>osmotic pressure only depends upon the concentration of the solution,</mark> but not upon the nature of the solute. Hence, osmotic pressure is a colligative property.

8.8.10 Thermodynamic treatment of osmotic pressure:

Osmotic pressure is related to the vapour pressures of the solution and the solvents by a well known equation in thermodynamics

$$\pi = \frac{RT}{V_1^0} \ln \frac{P^0}{P} \qquad \cdots\cdots (1)$$

Here,

$$\pi = \text{Osmotic pressure of solution}$$
$$T = \text{Temperature}$$
$$V_1^0 = \text{Molar volume of the solvent}$$
$$P^0 = \text{Vapour pressure of pure solvent}$$
$$P = \text{Vapour pressure of solution}$$

Rearranging

$$\pi V_1^0 = RT \ln \frac{P^0}{P} \qquad \cdots\cdots (2)$$

According to Raoult's law,

$$\frac{P}{P^0} = X_1$$

$$X_1 + X_2 = 1$$

So, $$1 - X_2 = X_1$$

Hence, $$\frac{P}{P^0} = 1 - X_2$$

So, $$\ln \frac{P}{P^0} = \ln(1 - X_2)$$

or, $$\ln \frac{P^0}{P} = -\ln(1 - X_2)$$

Putting in equation (2)

$$\pi V_1^0 = -RT \ln(1 - X_2) \qquad \cdots\cdots (3)$$

$$\ln(1 - X_2) = -X_2 + \frac{X_2^2}{2!} - \frac{X_2^3}{3!} \cdots\cdots$$

Since, solution is dilute and value of X_2 is very smaller than unity, so, X_2^2 and X_2^3 are neglected.

$$\therefore \quad \ln(1 - X_2) = -X_2$$

Putting this value in equation (3)

$$\pi V_1^0 = RT X_2 \qquad \qquad \cdots\cdots (4)$$

Since $\qquad X_2 = \dfrac{n_2}{n_1 + n_2}$

In the case of dilute solution, 'n_2' can be ignored in the denominator. So,

$$X_2 = \dfrac{n_2}{n_1}$$

Hence, equation (4) can be written as,

$$\pi V_1^0 = RT \dfrac{n_2}{n_1}$$

$$\pi V_1^0 n_1 = RT n_2$$

$\therefore$ Let $\qquad n_1 V_1^0 = V$

Where 'V' is the total volume of the solvent.

Hence, $\qquad \pi V = n_2 RT \qquad \qquad \cdots\cdots (5)$

According to equation (5), volume of the solvent 'V' can be taken as the volume of the solution, because solution is very dilute 'n_2' is the number of moles of solute

$$\pi V = \dfrac{W_2}{M_2} . RT \qquad \qquad \cdots\cdots (6)$$

With the help of equation (6), we can calculate the molar mass of the non-volatile, non-electrolyte solute in a volatile solvent. For this purpose, we should know the osmotic pressure of the solution 'π', volume of the solution 'V', weight of the solute W_2 and temperature of the solution 'T'. These equation (5) and (6) are called Van't Hoff's equations of osmotic pressure. It has another shape as well

$$\pi V = n_2 RT$$

$$\pi = \dfrac{n_2}{V} RT$$

$\therefore \qquad \dfrac{n_2}{V} = C \qquad$ (concentration in mol. dm^{-3})

$$\pi = C . RT \qquad \qquad \cdots\cdots (7)$$

$$\pi \propto C \qquad \text{(at const. temperature)}$$

It means that different solutions of same concentration will have same osmotic pressure at a given temperature.

EXAMPLE (8)

A solution of sucrose is prepared by dissolving 68.4 g of it in one dm of solution. What is it osmotic pressure at 300 K? The molar mass of sucrose is 342 g mol^{-1}.

$$R = 0.082 \ dm^3 \ atm \ K^{-1} \ mole^{-1}.$$

SOLUTION:

Data:

Mass of sucrose	=	68.4 g
Vol. of solution	=	1 dm^3
Temp.	=	300 K
Molar mass	=	342 g mol^{-1}
R	=	0.0821 dm^3 atm. K^{-1} mol^{-1}

Formula:

The formula for osmotic pressure (π) is

$$\pi = \frac{n_2}{V} RT$$

Mass of sucrose in 1 dm^3 of solution = 68.4 g

Molecular mass of sucrose = 342

Moles of sucrose, $n_2 = \dfrac{68.4}{342} = 0.2$ moles

The value of R is taken such that the units of pressure should be in atmospheres.

Substituting the values

$$\pi = \frac{0.2 \text{ moles} \times 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{1 \text{ dm}^3} = \boxed{4.92 \text{ atms.}} \quad \text{Ans.}$$

EXAMPLE (9)

An aqueous solution of glucose ($C_6H_{12}O_6$) has an osmotic pressure of 2.72 atmospheres at 298 K. How many moles and grams of glucose are dissolved dm^{-3} of the solution; R = 0.082 dm^3 atm K^{-1} mol^{-1}.

SOLUTION:

Data:

$$\pi = 2.72 \text{ atm}$$
$$\pi = 298 \text{ K}$$
$$n_2 = ?$$

Formula:

We know the relation for osmotic pressure

$$\pi = \frac{nRT}{V}$$

$$\pi V = n_2 RT$$

n_2 = number of moles of solute dissolved

$$n_2 = \frac{\pi V}{RT}$$

Substituting the values, we get

$$n_2 = \frac{2.72 \text{ atm} \times 1 \text{ dm}^3}{0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 0.12 \text{ moles}$$

Mass of glucose = 0.12×180 = $\boxed{21.6 \text{ g}}$ Ans.

EXAMPLE (10)

Osmotic pressure of solution containing 7 g of dissolved protein in 100 cm^3 of solution is 25 torr at body temperature 37°C. Calculate the molecular mass of the protein. $R = 0.082 \, dm^3 \, atm \, K^{-1} \, mol^{-1}$.

SOLUTION:

Data:

Mass of protein $= 7 \, g$

Vol. of solution $= 100 \, cm^3 = 0.1 \, dm^3$

Osmotic pressure, π $= 25 \, torr = \dfrac{25}{760} = 0.03289 \, atm.$

Temperature $= 37 \, C° + 273 = 310 \, K$

Formula:

We know that relation

$$\pi V = n_2 \, RT$$

Since, $n_2 = \dfrac{W}{M}$

So, $\pi V = \dfrac{W}{M} RT$

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

Substituting the values, we get

Molecular mass of protein $(M) = \dfrac{7 \, g \times 0.082 \, dm^3 \, atm \, K^{-1} \, mol^{-1} \times 310 \, K}{0.1329 \, atm \times 0.1 \, dm^3}$

$$M = \boxed{13389.01 \, g \, mol^{-1}} \quad \text{Ans.}$$

EXAMPLE (11)

A 5.13 % solution of sucrose $(C_{12}H_{22}O_{11})$ is isotonic with a 0.9 % solution of an unknown solute. Calculate the molar mass of unknown solute.

SOLUTION:

Data:

5.13 % solution means that 5.13 g of solute is dissolved in 100 cm^3 of solution.

Mass of sucrose $(W) = 5.13 \, g$

Molar mass of sucrose $(M) = 342 \, g \, mol^{-1}$

Volume of solution $(V) = 100 \, cm^3 = 0.1 \, dm^3$

Formula:

$$\pi V = n_2 RT$$

$$\pi = \dfrac{n_2 RT}{V}$$

Since, $n_2 = \dfrac{W}{M}$

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

Putting values

$$\pi = \frac{5.13 \, RT}{342 \times 0.1}$$

For unknown solute

Mass of solute	(W)	=	0.9 g
Molar mass of solute	(M)	=	?
Volume of solute	(V)	=	0.1 dm^3

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

$$\pi = \frac{0.9 \, RT}{M \times 0.1}$$

Since solutions are isotonic, so osmotic pressures must be the same.

Hence,

$$\frac{0.9 \, RT}{M \times 0.1} = \frac{5.13 \, RT}{342 \times 0.1}$$

$$M = \frac{0.9 \times 342}{5.13} = \boxed{60 \text{ gm mol}^{-1}} \text{ Ans.}$$

8.8.11 Mechanism of action of semipermeable membrane:

Various theories have been proposed from time to time, regarding the selective action of semipermeable membrane.

(i) Molecular sieve theory:

This concept was given by Traube. He thought that each semipermeable membrane is consisted of tiny pores, which allow the passage of smaller solvent molecules only. But larger solute particles are retained. But it is very strange to know that if the solvent molecules are bigger than the solute, then again the molecules of solvents pass through. Hence, this theory is not widely accepted.

(ii) Adsorption theory:

According to this theory there happens preferential adsorption of solvent molecules on the surface of the membrane. Due to their closeness to the pores of the membrane, they can pass through easily.

(iii) Concept of capillary action:

According to this theory, it is thought that any semipermeable membrane is consisted of large number of microscopic capillaries, which are not wetted by the solvent. The vapours of the solvent can pass through these from a region of high vapour pressure to a region of low vapour pressure. Vapour pressure on the solvent side is greater than on the solution side. Anyhow, this theory has the weakness that the wetting behaviour of the membrane can hardly justify this theory.

8.9.0 ABNORMAL COLLIGATIVE PROPERTIES

We have mentioned four colligative properties and all of them give us the expression with the help of which molar masses of the solutes can be determined. In some cases, the molar masses determined by these methods do not agree with theoretical values. Reason is that, the molecules of such compounds either dissociate or associate.

In the case of dissociation of solute particles, the number of particles in the solution increase and so the colligative properties increase. In the case of association of the solute particles, the number of particles in the solution decrease and so the colligative properties decrease.

The formulas for the determination of molar masses from the colligative properties are as follows:

Since, $\dfrac{\Delta P}{P^o} = \dfrac{W_2}{M_2} \times \dfrac{M_1}{W_1}$

So, $\Delta P \propto \dfrac{1}{M_2}$ ...... (1)

Since, $\Delta T_b = K_b \cdot \dfrac{1000 \, W_2}{W_1 \times M_2}$

So, $\Delta T_b \propto \dfrac{1}{M_2}$ ...... (2)

Since, $\Delta T_f = K_f \cdot \dfrac{1000 \, W_2}{W_1 \times M_2}$

So, $\Delta T_f \propto \dfrac{1}{M_2}$ ...... (3)

Since, $\pi V = \dfrac{W_2}{M_2} RT$

$\pi \propto \dfrac{1}{M_2}$ ...... (4)

From all these expressions (1) to (4), we come to know that a colligative property is inversely proportional to the molar mass of the solute.

$$\text{Colligative propertty} \propto \frac{1}{\text{Molar mass}}$$

$$\text{Molar mass} \propto \frac{1}{\text{Colligative property}}$$

The colligative property is directly proportional to the number of solute particles.

Hence, $\text{Molar mass} \propto \dfrac{1}{\text{Number of solute particles}}$ ...... (5)

8.9.1 Association:

Some of the organic substances undergo association in non-aqueous solvents, so the total number of the molecules in the solution decrease. Association may be due to hydrogen bonding. When the dimers of solute molecules are produced, then the number of solute particles become half and molar mass becomes double, than that of its theoretical values.

In the case of CH_3COOH, the molar mass comes out to be 120 rather than 60, which is its actual value and the reality is that CH_3COOH forms the dimer in benzene.

8.9.2 Dissociation:

If the solute under consideration is electrolyte like an acid, base or a salt, the number of particles increase. So the molar masses decrease.

NaCl gives double the number of particles, so the molar mass become close to 30 which is approximately half of 58.5. In the case of $CaCl_2$, the number of particles become thrice and so the molar mass becomes almost $\frac{1}{3}$ of its actual molar mass.

8.9.3 Van't Hoff factors (i):

As we have discussed above that the values of the colligative properties are higher for solutions of electrolytes and the values of colligative properties are less for the compound making the dimers. In the case of non-electrolyte the colligative properties are quite normal.

The number of times, a colligative property of electrolyte is greater than that of non-electrolyte of same concentration is called Van't Hoff factor (i). It can be written as a ratio

$$i = \frac{\text{Observed value of colligative property of an electrolyte}}{\text{Observed value of colligative property of non-electrolyte}}$$

If the colligative property of electrolyte is denoted by dash (/).

$$\text{Then, } i = \frac{\Delta P'}{\Delta P^\circ} = \frac{\Delta T'_b}{\Delta T^\circ_b} = \frac{\Delta T'_f}{\Delta T^\circ_f} = \frac{\pi'}{\pi^\circ} \quad \cdots\cdots (6)$$

It is also observed that, the colligative properties increase with increasing dilution and approach limiting value at very large dilutions.

Van't Hoff factor helps us to determine the degree of dissociation of the electrolyte.

8.9.4 Degree of dissociation from colligative properties:

We consider one mole of an electrolyte and suppose that 'α' moles from this dissociates to form the ions. The undissociated number of moles is '$1 - \alpha$'. Suppose that 'n' is the number of ions formed when one mole of the solute dissociates, then the number of solute particles after the dissociation of same quantity is '$1 - \alpha + n\alpha$'.

Now,

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

We know that, according to definition of Van't Hoff (i) factor

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

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

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

$$i - 1 = n\alpha - \alpha$$

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

$$\alpha = \frac{i - 1}{n - 1} \qquad \cdots \cdots (7)$$

This equation is very important because we can calculate the degree of dissociation of electrolyte if we know the 'i' factor and the number of possible ions produced due to the dissociation of one molecule of the electrolyte.

EXAMPLE (12)

A substance "A" of molar mass, 98 associates as $2A \rightleftharpoons A_2$, when it is dissolved in CCl_4. If 10 g of A is dissolved in 2 kg of CCl_4, the freezing point is lowered by 1.08°C. K_f for CCl_4 is 31.8 K. Calculate the degree of association of A.

SOLUTION:

Data:

First of all do the calculations of molecular mass which can be obtained according to the data.

$$W_2 = 10 \text{ g}$$
$$W_2 = 2000 \text{ g}$$
$$\Delta T_f = 1.08 \text{ °C}$$
$$K_f = 31.8 \text{ Km}$$

Formula:

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

Putting values

$$M_2 = \frac{31.8 \text{ K mol}^{-1} \times 10 \text{ g} \times 1000 \text{ g}}{1.08 \text{ K} \times 2000 \text{ g}} = \boxed{147.2 \text{ g mol}^{-1}} \quad \text{Ans.}$$

Calculation of Van't Hoff factor "i"

$$i = \frac{\text{normal molar mass}}{\text{observed molar mass}} = \frac{98}{147.2} = 0.6657$$

Calculation of degree of association (α)

$$\alpha = \frac{i - 1}{\dfrac{1}{m} - 1}$$

Since 'A' undergoes dimerization, so $m = 2$

$$\alpha = \frac{0.6657 - 1}{\frac{1}{2} - 1} = \frac{0.6657 - 1}{0.5 - 1} = \frac{-0.3342}{-0.5} = 0.668$$
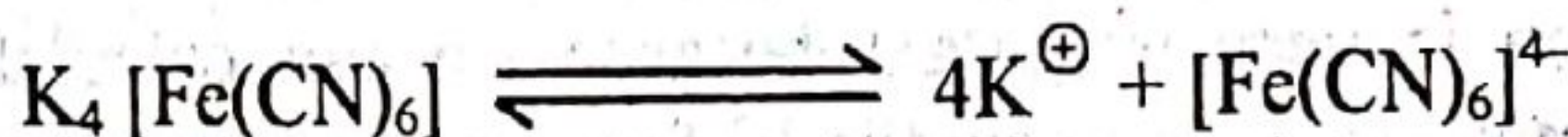
So, $\boxed{\alpha = 66.8\%}$

So, 66.8 % of the molecules of A are associated to give the dimer.

EXAMPLE (13)

When $K_4 Fe(CN)_6$ is dissolved in water, then it is 50 % dissociated, having concentration of solution as 0.1 M. What is the osmotic pressure of this solution.

SOLUTIONS:

Data:

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

Since one molecule dissociation into five particles

$$m = 5$$

Degree of dissociation

$$a = 50\% \text{ or } 0.5$$

Formula:

Degree of dissociation α is given by the equation

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

Putting values

$$0.5 = \frac{i - 1}{5 - 1}$$

$$i - 1 = 4 \times 0.50 = 2$$

Van't Hoff factor

$$i = 2 + 1 = 3$$

Formula:

The equation for osmotic pressure is

$$\pi = i\,CRT$$

$$C = 0.1 \text{ moles dm}^{-3}$$
$$R = 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$
$$T = 300 \text{ K}$$

Putting the values

$$\pi = 3 \times 0.1 \text{ moles dm}^{-3} \times 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{mol}^{-1} \times 300 \text{ K}$$

$$\boxed{\pi = 7.38 \text{ atms.}}$$

EXAMPLE (14)

1 % solution KCl is dissociated to the extent of 80 %. What will be the osmotic pressure at 300 K? $R = 0.082 \text{ dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$.

SOLUTION:

Data:

Mass of the solute	$= 1$ g
Volume of the solution	$= 100$ ml (since solution is 1 %)
Mass of the solute dm^{-3}	$= 10$ g
Molar mass of KCl	$= 74.5$ g mol^{-1}

If the solution would have been in 1 dm³ of volume, then 10 g would have been dissolved in 1000 cm³ of solution

So, molar conc. of solution (s) $= \dfrac{10}{74.5} = 0.1342$ moles dm⁻³

Temperature $= 27°C + 273 = 300$ K

Formula:

The formula for osmotic pressure

$$\pi = CRT \qquad (C = \text{molar concentration})$$

Putting values

$$\pi = 0.1342 \text{ moles dm}^{-3} \times 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}$$
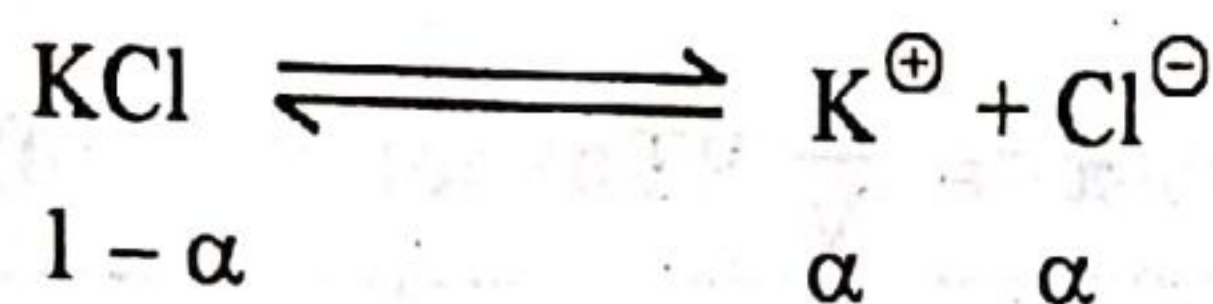
$$\pi = 3.3 \text{ atm}$$

This is the osmotic pressure of KCl if it would not have dissociated. It is the normal osmotic pressure

$$\text{Van't Hoff factor} \quad (i) = \dfrac{\text{observed osmotic pressure}}{\text{normal osmotic pressure}}$$

The Van't Hoff factor 'i' can be calculated from the degree of dissociation

Let us say the degree of dissociation of KCl is α

$$KCl \rightleftharpoons K^{\oplus} + Cl^{\ominus}$$
$$1 - \alpha \qquad\qquad \alpha \quad\; \alpha$$

Number of moles before dissociation $= 1$

Number of mole after dissociation $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

Now, $\alpha = 0.8$, because KCl is 80 % dissociated

Van Hoff factor

$$i = \dfrac{\text{Total no. of moles after dissociation}}{\text{Total no. of moles before dissociation}}$$

$$i = \dfrac{1 + \alpha}{1}$$

$$i = \dfrac{1 + 0.8}{1}$$

$$i = 1.8$$

Now

$$i = \dfrac{\text{observed osmotic pressure}}{\text{normal osmotic pressure}} = 1.8$$

$$\dfrac{\text{Observed osmotic pressure}}{3.3} = 1.8$$

or Observed osmotic pressure $= 3.3 \times 1.8 = \boxed{5.94 \text{ atm.}}$ Ans.

EXAMPLE (15)

Sodium chloride is dissolved in water and contains 5.85 g dm^{-3}. The osmotic pressure is 4.74 × 10^5 Nm^{-2} at 300 K. Calculate its Van't Hoff factor and degree of dissociation of NaCl.

SOLUTION:

Data:

Observed pressure (π)   = 4.74 × 10^5 Nm^{-2}

Mass of NaCl   = 5.85 g

$\therefore$ Mol mass of NaCl   = 58.5 g mol^{-1}

No. of moles of NaCl   = $\dfrac{5.85}{58.5}$ = 0.1

$$T = 300 \text{ K}$$
$$V = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$$
$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

Formula:

$$\pi V = nRT$$
$$\pi = \frac{n}{V} RT$$

Putting values

$$\pi = \frac{0.1 \text{ moles} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{10^{-3} \text{ m}^3}$$

$$\pi = 2.49 \times 10^5 \text{ Nm}^{-2}$$

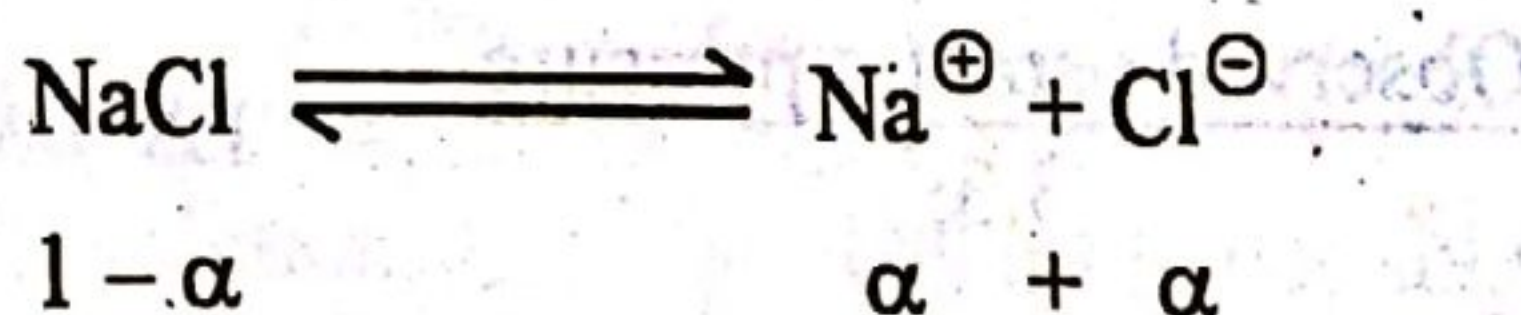$$\boxed{\begin{array}{l} J = \text{kg m}^2 \text{ s}^{-2} \\ N = \text{kg m s}^{-2} \end{array}}$$

This osmotic pressure is created when NaCl is thought to be normal

Van't Hoff factor   i   = $\dfrac{\text{observed osmotic pressure}}{\text{calcualted or normal osmotic presure}}$

$$i = \frac{4.74 \times 10^5}{2.49 \times 10^5} = 1.90$$

In order to calculate the degree of dissociation 'α', proceed as follows:

Let "α" be the degree of dissociation of NaCl

$$NaCl \rightleftharpoons Na^\oplus + Cl^\ominus$$

$$1 - \alpha \qquad\qquad \alpha + \alpha$$

Number of moles before dissociation   = 1

Number of moles after dissociation $= 1 - \alpha + \alpha + \alpha$

$$= 1 + \alpha$$

$$i = \frac{\text{Total no. of moles after dissociation}}{\text{Total no. of moles before dissociation}}$$

$$1.9 = \frac{1 + \alpha}{1}$$

$$1 + \alpha = 1.9$$

$$\boxed{\alpha = 0.9}$$

$\boxed{\text{Thus the degree of dissociation of NaCl is} = 90\%}$ Ans.

8.9.5 Effect of dilution on degree of dissociation:

It is clear that when the dilution of the solution is increased, then the degree of dissociation increases. When the solution is infinitely dilute then there is 100 % dissociation and 'α' becomes unity. Look at the table (6) for different electrolytes. It is clear that in the case of concentrated solution around one molal, the Van't Hoff factor (i) is less than that value which is there in the case of complete dissociation at infinite dilution.

Table (6) 'i' factor and concentration of solutions

Electrolyte	Extrapolated values (i) 0.00 m	(i) 0.01 m	(i) 0.1 m	(i) 1.0 m
NaCl	2	1.94	1.87	1.82
HCl	2	1.94	1.89	2.12
CuSO$_4$	2	1.45	1.12	0.93
CaCl$_2$	3	2.70	2.60	2.03
H$_2$SO$_4$	3	2.46	2.12	2.17
Pb(NO$_3$)$_2$	3	2.63	2.13	1.31
FeCl$_3$	4	3.72	3.22	2.40

The value of 'i' for uni-univalent electrolyte as NaCl should be 2 because the double the number of particles are produced and so we expect that the freezing point of one molal NaCl solution should be lowered twice as compared one molal solution of non-electrolyte. But this is not true in the table for 0.01 molal, 0.1 molal and 1 molal because at these concentrations, 100 % dissociation of NaCl is not possible. When NaCl is 1.00 molal then 'i' factor is 1.82 rather than 2.

Similar types of explanations can be given for CaCl$_2$ and FeCl$_3$ etc.

8.10.0 DISTRIBUTION LAW

8.10.1 Introduction:

In order to understand the distribution law, let us consider two immiscible liquids called 'A' and 'B'. When they are mixed, two layers are produced. The liquid with higher density makes the lower layer.

Now take a solid solute 'X' of such a nature, that it is soluble in both 'A' and 'B'. The substance 'X' is distributed in two layers. Definite concentration of the substance 'X' are present in separate layers of 'A' and 'B'. These concentrations depend upon the solubilities of 'X' in solvents 'A' and 'B'.

8.10.2 State of dynamic equilibria:

At a constant temperature, the concentration of 'X' in both layers of 'A' and 'B' remain constant. Anyhow, the molecules of 'X' travel from 'A' to 'B' and 'B' to 'A' with equal rates. This is a state of dynamic equilibria. Fig. (23)
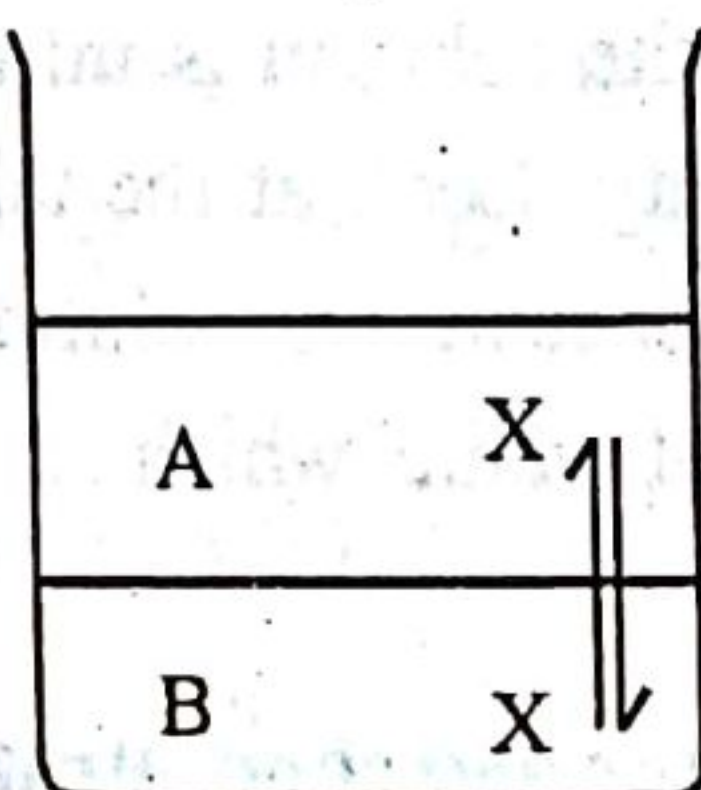

Fig. (23) Dynamic equilibria of solte in two layers.

Experimentally it is found that the ratio of concentration 'X' in 'A' and 'B' is a constant quantity at a given temperature. This constant parameter is called distribution co-efficient or partition co-efficient and is denoted by K_D.

$$K_D = \frac{\text{concentration of 'X' in 'A'}}{\text{concentration of 'X' in 'B'}}$$

Example:

(i)   Succinic acid is soluble in water and ether both. Anyhow, it is more soluble in water than ether. Fig. (24)
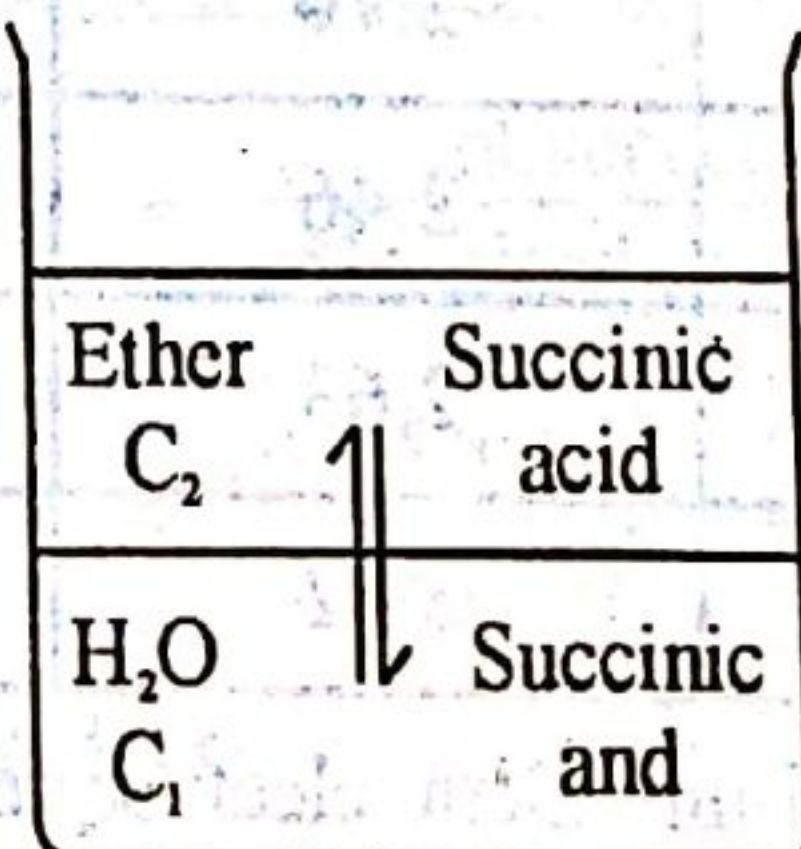

Fig. (24) Distribution of succine acid in water and ether.

Following table (7) shows the concentrations of succinic acid in ether and water and the distribution co-efficient of succinic acid in these two solvents.

$$K_D = \frac{\text{conc. of succinic and in water}}{\text{conc. of succinic acid in ether}}$$

TABLE (7): Distribution of succinic acid in water and ether.

Concentration of succinic acid in 10 cm^3 of water (C_1)	Concentration of succinic acid in 10 cm^3 of ether (C_2)	$K_D = \dfrac{C_1}{C_2}$
0.024	0.0046	5.2
0.069	0.013	5.2
0.119	0.022	5.2
0.164	0.031	5.2

Distribution of I_2 between water and CS_2 is another best example. Following table (8) helps to understand the constancy of K_D. The C_1 and C_2 are the concentrations of I_2 in 10 cm^3 of solvent.

TABLE (8): Distribution of I_2 in water and CS_2.

I_2 in CS_2 (C_1)	I_2 in H_2O (C_2)	$K_D = \dfrac{C_1}{C_2}$
1.74	0.0041	420
1.29	0.0032	420
0.66	0.0016	420

8.10.3 Nernst's Distribution law:

In 1891, Nernst studied the distribution of several solutes in suitable pairs of solvents. On the basis of his findings, he gave a law which is called Nernst's distribution law or Nernst's partition law. It is also called distribution law or partition law.

Definition:

"If a solute distributes itself between two immiscible solvents at constant temperature and the molecular conditions of the solute remain the same, then the distribution co-efficient, K_D, remains constant at a given temperature for various concentrations of solutions."

8.10.4 Solubility and distribution law:

If a solute is mixed with a pair of immiscible solvents, then we can add the solute in such a quantity, that the solutions may be saturated. The saturated solutions of the solutes are indirectly the solubilities of the solute in two solvents.

$$K_D = \frac{C_A}{C_B} = \frac{S_A}{S_B}$$

Where 'S_A' and 'S_B' are the solubilities of solutes in 'A' and 'B'. It means that, we can calculate the solubility of the solute in one of the solvents 'A' or 'B' if we know the solubility in the other solvent and the value of K_D.

8.10.5 Limitations of distribution law:

As we have mentioned above, the distribution law is not applicable for all the solutes for every pair of liquids. Following conditions should be fulfilled for the application of this law.

(i)   The concentrations of the solute in two solvents should be measured after the equilibrium has been established at a given temperature.

(ii)   The solution should be dilute. Concentrated solutions mostly donot obey this law.

(iii)   The solvents should be non miscible or only slightly miscible.

(iv)   The temperature should be constant during the experiment.

(v)   The solute should be neither associated nor dissociated. In other words the molecular state of the solute should be the same in two solvents.

8.10.6 Modification of distribution law and change in the molecular state:

According to the above discussion, the ratio of 'C_1' and 'C_2' is a constant factor. Anyhow, the solute should neither be associated nor dissociated in any of the liquids 'A' and 'B'. If the solute changes its molecular state, then it is found that ratio 'C_1' to 'C_2' is not constant. But keep in mind that distribution law will be applicable to those concentrations which are in the normal state.

Let us discuss, the situation of association and then dissociation in any one of the solvents 'A' or 'B'.

8.10.7 Association of solute:

We have two solvents 'A' and 'B' which are immiscible. Our solute is 'X' which distributes in 'A' and 'B'. Suppose that solute 'X' is present as simple molecules in solvent 'A'. If 'n', molecules of 'X' are associated in solvent 'B' than 'X_n' molecules are present in solvent 'B'. Keep it in mind that some molecules of 'X' are present as simple molecules along with 'X_n' in solvent 'B'. The reason is that, it is not necessary that all the molecules of 'X' get associated. There is equilibrium between 'nX' and 'X_n' and definitely there is equilibrium constant. Fig. (25)
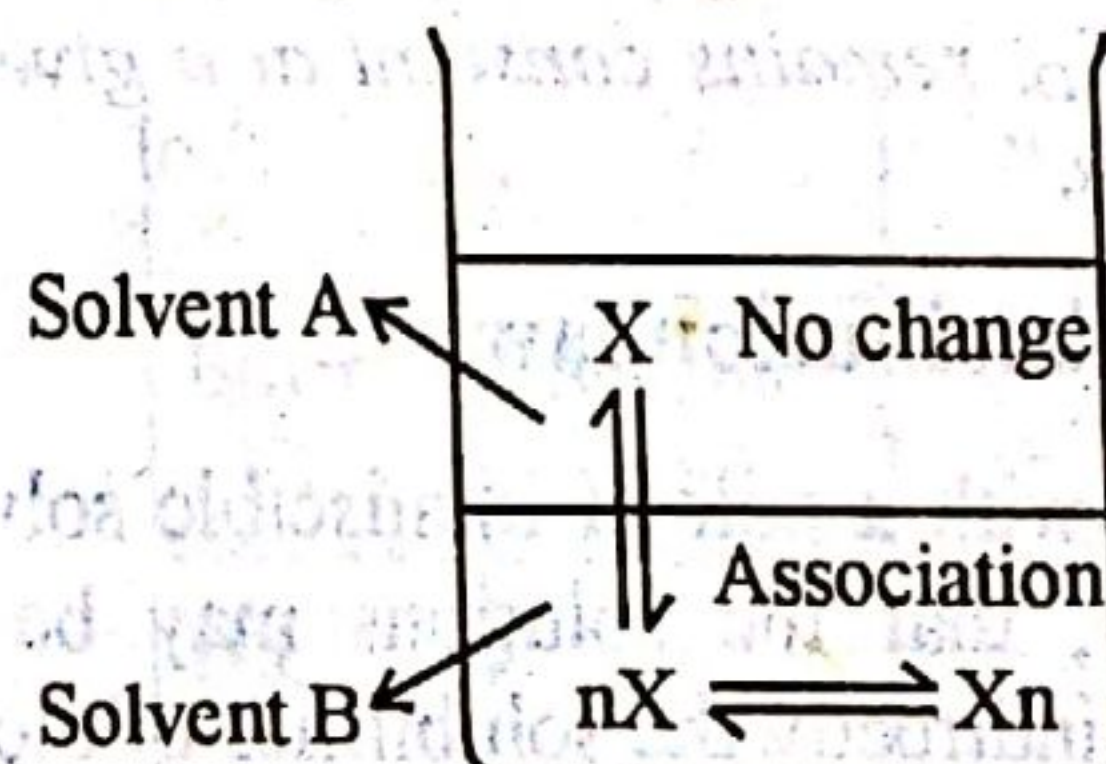

Fig. (25) Distribution coefficient when association happens in one of the solvents.

C_1 = Concentration of 'X' in 'A'
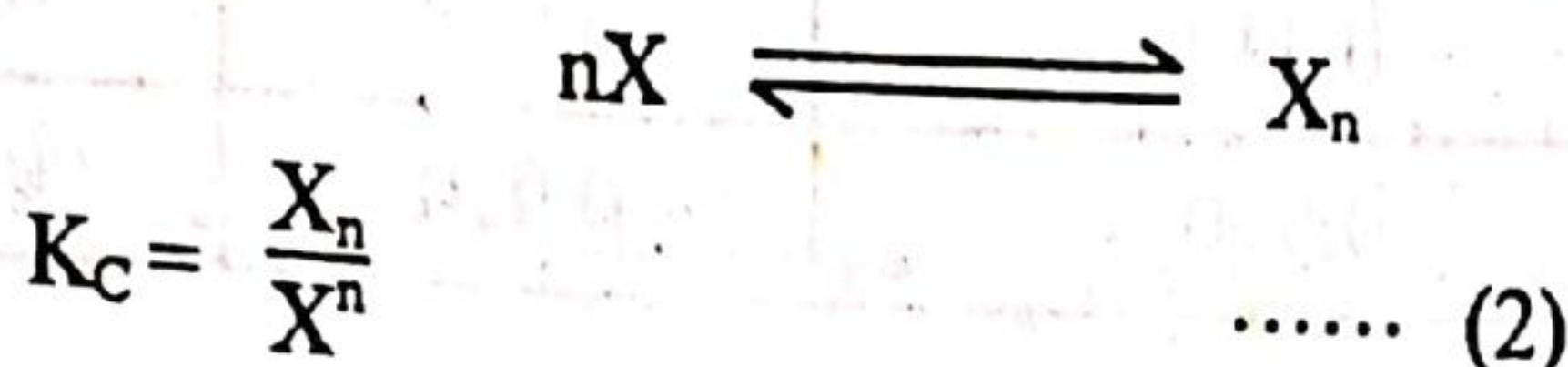
C_3 = Concentration of 'X' in 'B'

C_2 = Concentration of 'X_n' in 'B'

Distribution law can be applied for 'C₁' and 'C₃' in solvents 'A' and 'B'

$$K_D = \frac{C_1}{C_3} \qquad \cdots\cdots (1)$$

There is a chemical equilibrium between 'nX' and 'X$_n$' in solvent 'B'. The equilibrium constant can be written as follows:

$$nX \rightleftharpoons X_n$$

$$K_C = \frac{X_n}{X^n} \qquad \cdots\cdots (2)$$

'X' corresponds to 'C₃' and 'X$_n$' corresponds to 'C₂', so

$$K_C = \frac{C_3^n}{C_2} \qquad \cdots\cdots (3)$$

Let us take the nth root of equation (3)

$$K_C^{1/n} = \frac{C_3}{C_2^{1/n}} \qquad \cdots\cdots (4)$$

Dividing equation (1) with equation (4)

$$\frac{K_D}{K_C^{1/n}} = \frac{C_1}{C_2^{1/n}}$$

$$K_D = \frac{C_1}{C_2^{1/n}} \qquad \cdots\cdots (5)$$

So, when the solute is associated in one of the solvents, then the value of K_D is not the simple ratio of 'C₁' and 'C₂'. If two molecules of substance 'X' are associated, then n = 2

$$K_D = \frac{C_1}{\sqrt{C_2}}$$

If three molecules of the substance 'X' are associated, then

$$K_D = \frac{C_1}{C_2^{1/3}} \quad \text{and so on.}$$

Anyhow, if the solute 'X' is associated in solvent 'B' and 'n' molecules of that are associated, then

$$K_D = \frac{C_1}{C_2^{1/n}}$$

Example:

One of the best examples is the distribution of benzoic acid in water and benzene. Benzoic acid is dimerized in benzene and so the value of 'n' is 2. Table (9) shows the concentrations in two phases.

$$K_D = \frac{\sqrt{C_{benzene}}}{C_{water}}$$

Table (9) Distribution of benzoic acid in water and benzene

In water (C_1)	In benzene (C_2)	$K = \dfrac{C_1}{C_2}$	$K_D = \dfrac{C_1}{\sqrt{C_2}}$
0.0150	0.242	0.062	0.0305
0.0195	0.412	0.048	0.0304
0.0289	0.970	0.030	0.0299

8.10.8 Dissociation of solute:

There are certain solutes which are dissociated into ions in one of the solvents 'A' and 'B'. Under these circumstances the ratio C_1/C_2 does not remain constant.

Suppose in solvent 'A' the concentration of 'X' is 'C_1' and in solvent 'B' the concentration of 'X' is 'C_2'. Remember that, C_2 is the total concentration of 'B' including dissociated and undissociated molecules. Now suppose the degree of dissociation of 'X' in 'B' is 'α'. It means that out of one mole of 'X', 'α' has been dissociated. '$1 - \alpha$' is left behind as undissociated. Fig. (26)

$$X \rightleftharpoons \text{dissociated}$$
$$1 \qquad\qquad 0$$
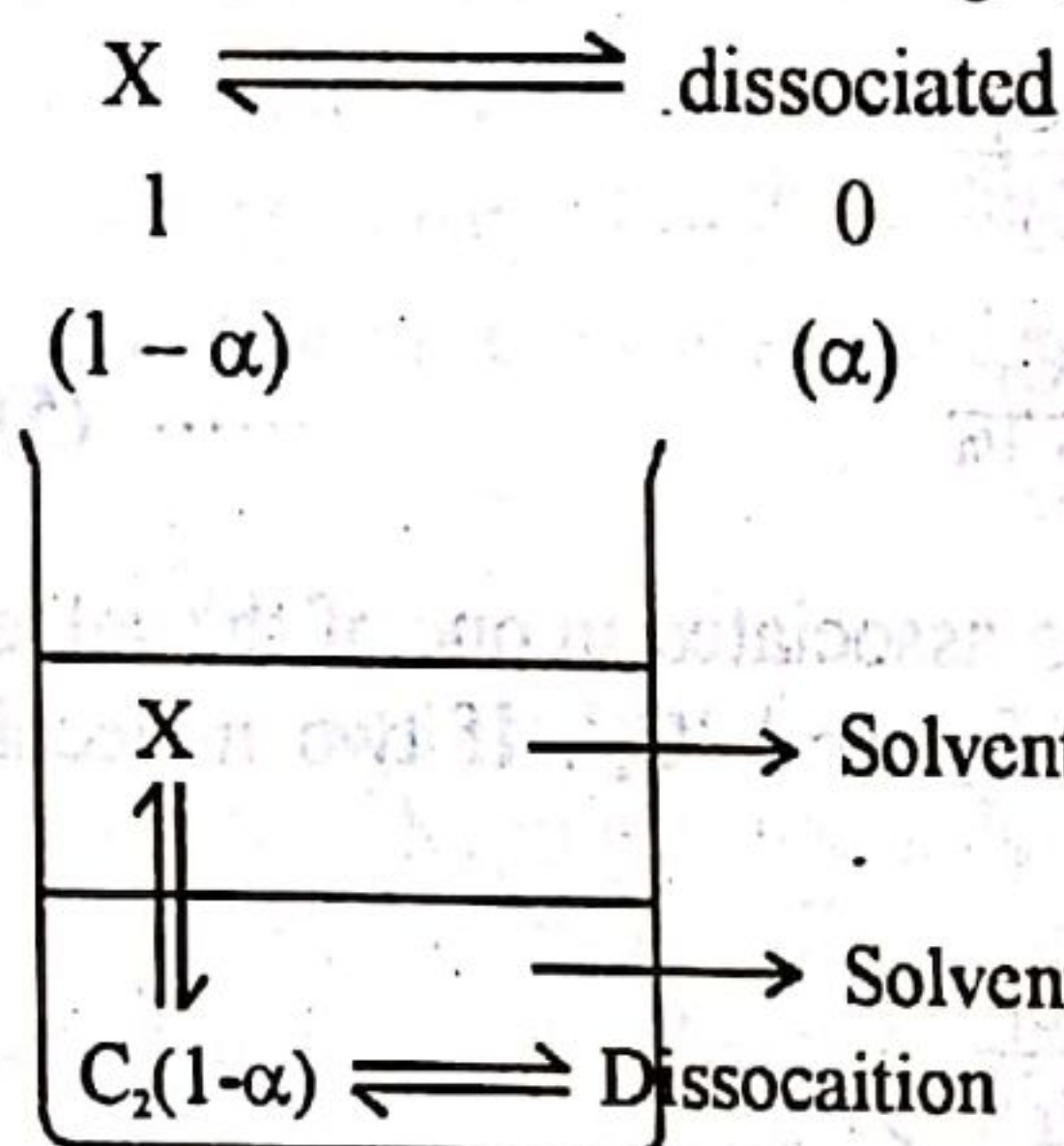$$(1 - \alpha) \qquad (\alpha)$$

Fig. (26) Dissociation of solute in solvent B.

The concentration of undissociated or normal molecules in solvent 'B' will be $C_2 (1 - \alpha)$. The distribution law is applicable to normal molecules. So

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

In other words, the K_D can be calculated, if we know the 'C_1' and 'C_2' and degree of dissociation.

Examples:

When succinic acids or oxalic acid are allowed to be distributed in ether and water, then we come to know that, these acids dissociate in water to some extent. So, the above equation will hold.

How to measure 'α':

The degree of dissociation 'α' in the given solvent can be found by measuring electrical conductance of the solution in water.

EXAMPLE (16)

Benzoic acid distributes itself between water and benzene in such a way that in a definite volume of water, there are 1.50, 1.95 and 2.97 g of benzoic acid; while in equal volume of benzene, there are 24.2, 41.2 and 97.2 g of benzoic acid. What conclusion can be drawn from these results concerning the molecular condition of benzoic acid in benzene.

SOLUTION:

(i) First of all we suppose that benzoic acid is in normal state in both phases

Formula:

$$K_D = \frac{C_{Water}}{C_{Benzene}}$$

Putting the values of concentration of benzoic acid is both phases one by one

(i) $\dfrac{1.50}{24.2} = 0.06198$

(ii) $\dfrac{1.95}{41.2} = 0.04747$

(iii) $\dfrac{2.97}{97.2} = 0.00062$

Since ratio is not constant, so benzoic acid is not normal in any one of the solvents or both solvents.

(ii) Now consider that benzoic acid is associated in benzene and becomes a dimer.

Formula:

$$K_D = \frac{C_{Water}}{\sqrt{C_{Benzene}}}$$

Putting the values of concentrations again one by one

(i) $\dfrac{1.50}{\sqrt{24.2}} = \dfrac{1.50}{4.919} = 0.3049$

(ii) $\dfrac{1.95}{\sqrt{41.2}} = \dfrac{1.95}{6.418} = 0.3036$

(iii) $\dfrac{2.97}{\sqrt{97.0}} = \dfrac{2.97}{9.848} = 0.3016$

The ratio in the two above cases are fairly constant. Hence benzoic acid exists as dimmer i.e. $(C_6H_5COOH)_2$ in benzene.

EXAMPLE (17)

Benzoic acid is distributed between water and benzene calculate the molar mass of benzoic acid in benzene from the following data:

Conc. in aq layer (C_1)	0.3	0.6	0.9
Conc. in benzene layer (C_2)	1.0	4.0	9.0

SOLUTION:

Let us suppose that liquids remain normal in both phases:
Putting values in the formula

(i) $\dfrac{C_1}{C_2} = \dfrac{0.3}{1.0} = 0.3$

(ii) $\dfrac{C_1}{C_2} = \dfrac{0.6}{4.0} = 0.15$

(iii) $\dfrac{C_1}{C_2} = \dfrac{0.9}{9.0} = 0.1$

Since the ratio is not constant so, benzoic acid does not exist as single molecule in benzene. Suppose that the benzoic acid is associated in benzene.

Formula:

$$K_D = \dfrac{C_1}{\sqrt{C_2}}$$

$$K_D = \dfrac{C_1}{\sqrt{C_2}} = \dfrac{0.3}{\sqrt{1.0}} = 0.3$$

$$K_D = \dfrac{C_1}{\sqrt{C_2}} = \dfrac{0.6}{\sqrt{4.0}} = 0.3$$

$$K_D = \dfrac{C_1}{\sqrt{C_2}} = \dfrac{0.9}{\sqrt{9.0}} = 0.3$$

Since $\dfrac{C_1}{\sqrt{C_2}}$ comes out to be constant, therefore, benzoic acid gives dimer in benzene. Hence molar mass of benzoic acid in benzene will be twice its normal mass.

New molar mass in benzene $= 2[C_6H_5COOH]$
$= 2[6 \times 12 + 5 \times 1 + 12 + 2 \times 16 + 1]$
$= \boxed{244 \text{ g mol}^{-1}}$ Ans.

8.10.9 Applications of distribution law:

There are numerous applications of distribution law. These applications are operative in the laboratory as well as in the industry. We are going to discuss a few of them.

(1) Solvent Extraction:

Organic substances present in aqueous solution can be extracted by organic solvents. The aqueous solution of the compound is shaken with an organic compound in which the solute is more soluble. Commonly used organic solvent in the laboratory is diethyl ether. Most of the organic substances pass to the ether layer during shaking. When it is allowed to stand, the ethereal layer separates out and water layer being heavier goes down. The lower aqueous layer is run out. The ethereal layer is distilled and organic compound is separated Fig. (27).

Some of the organic compound is still present in the aqueous layer according to its distribution co-efficient. By adding another lot of ether, it can be extracted, and by repeating this process, more and more organic compound can be transferred to ether and separation is completed.
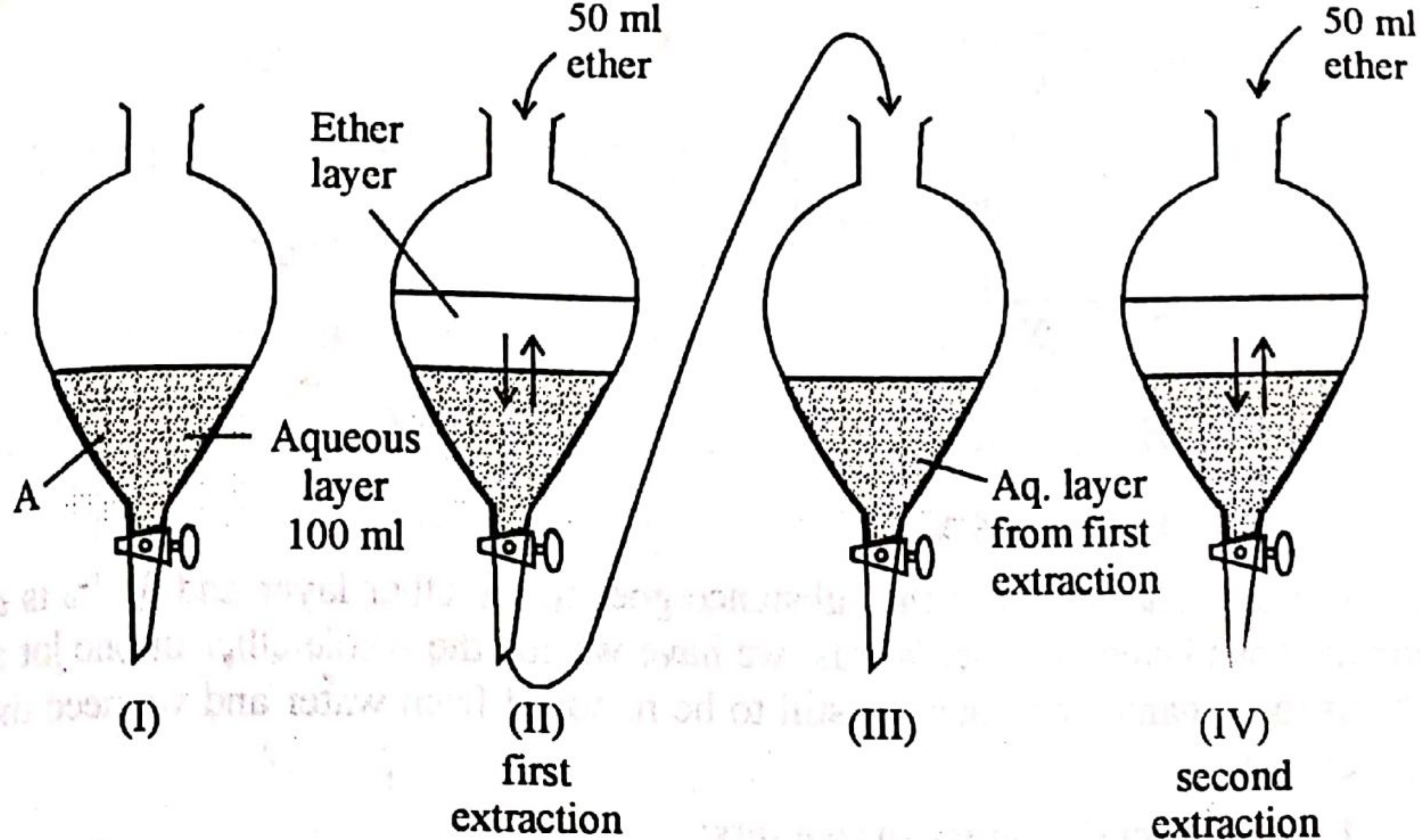
Fig. (27) Illustration of multiple extractions.
The given solvent (ether) is used in two successive portions.

Commonly used solvents:

In addition to ether, other solvents which are used for organic extraction from aqueous layers are hexane, benzene, chloroform, acetone, carbon disulphide etc.

Multiple extractions:

It is known fact that greater the distribution ratio in the favour of organic solvents, greater will be the amount extracted in any one operation. In order to recover the maximum amount of the substance from the aqueous solution, the extraction is made in two or more successive operations and by using small portions of the solvents.

Multiple extraction is a more efficient process, than doing the extraction in a single step.

Examples of multiple extraction:

Let us have 1000 cm³ of aqueous solution containing 'X' grams of organic substance. Suppose that we use ether as a organic solvent to extract organic compound. Moreover it is supposed that, the value of 'K_D' is 2. It means that the solubility of compound in ether is two times more favourable than water. Suppose we have 1000 cm³ of ether at our disposal to get the maximum amount of the organic substance from aqueous solution.

Now let us do the calculations with different possibilities.

(a) **Using 1000 cm³ of ether in one lot:**

Suppose 'H' gram of the organic substance from total 'X' grams, goes to the ether layer, then the amount of organic compound in the water layer is (X – H). So

$$\text{Concentration in ether layer} = \frac{H}{1000} \text{ g . cm}^{-3}$$

$$\text{Concentration in water layer} = \frac{X-H}{1000} \text{ g . cm}^{-3}$$

$$\text{Distribution coefficient} = K_D = 2$$

$$K_D = \frac{C_{ether}}{C_{water}}$$

$$2 = \frac{H}{1000} \Big/ \frac{X-H}{1000}$$

$$2 = \frac{H}{X-H}$$

$$H = \frac{2}{3} X$$

$$H = 0.66 X$$

It means that 66 % of the substance goes to the ether layer and 33 % is still in the aqueous layer. In other words, we have wasted the whole ether in one lot and 33 % of the organic compound is still to be removed from water and we need more ether for that.

(b) **Using 500 cm³ of ether in two lots:**

Now suppose that 'H_1' is the mass of the organic substance which goes to ether layer and $(X - H_1)$, remains in 1000 cm³ of water

$$K_D = \frac{C_{ether}}{C_{H_2O}}$$

$$2 = \frac{H_1}{500} \Big/ \frac{X-H_1}{1000}$$

$$H_1 = \frac{1}{2} X$$

$$H_1 = 0.5 X$$

In other words, 50 % of organic compound has been extracted from aqueous layer and we have 500 cm³ of ether at our disposal. This 500 cm³ of remaining ether is able to remove 50 % of the remaining 50 % organic compound from water. So, by using two installments 75 % of organic compound can be extracted.

(c) **Extraction in four instalment:**

Similar type of calculations tell us that if we use four instalmetns of ether by taking 250 cm³ at a time, then 80.2 % organic compound is extracted.

(d) **Extraction in five instalments:**

If we use five instalemtns of ether by taking 200 cm³ at a time, then 83.8 % compound can be extracted.

Is complete extraction possible?

It is not possible to remove whole of the dissolved substance, how much the large number of extractions may be.

(2) **Determination of association:**

Some of the solutes are associated in a particular solvent. If we know the distribution co-efficient and the concentration of the solute in two solvents, then we can calculate the value of 'n' in that particular solvent.

If the solute is associated in solvent 1 and the association is 'n' time, then

$$K_D = \frac{C_1^{1/n}}{C_2}$$

If the compound is associated in phase 2, 'n' time, then K_D is

$$K_D = \frac{C_1}{C_2^{1/n}}$$

Benzoic acid is associated in benzene but not in water, so

$$K_D = \frac{\sqrt{C_{benzene}}}{C_{aqueous}}$$

(3) Determination of dissociation:

If a solute is dissociated in phase 2, then the degree of dissociation 'α' can be calculated, when we know the values of K_D,

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

(4) Determination of solubility:

The solubilities correspond to the concentrations in two layers. Hence

$$K_D = \frac{C_1}{C_2} = \frac{S_1}{S_2}$$

Suppose we want to determine, the solubility of iodine in benzene. Shake iodine with water and benzene. From the above equation, if we know the solubility of iodine in water, then solubility in benzene can calculated

$$K_D = \frac{S_B}{S_W}$$

(5) Determination of distribution co-efficient of iodine:

Iodine is shaken with water and benzene in a bottle. Iodine distributes itself in two layers. The concentration of iodine in the each layer is determined by titration with standard solution of $Na_2S_2O_3$.

$$K_D = \frac{\text{concentration of } I_2 \text{ in } H_2O}{\text{concentration of } I_2 \text{ in benzene}}$$

(6) Determination of equilibrium constant of I_3^- and I^-:

In order to understand this process, let us take a solution of KI having concentration 'a' in water. This solution is shaken with iodine in a beaker. Then benzene is added and it is shaken. Diagram (28) is as follows:
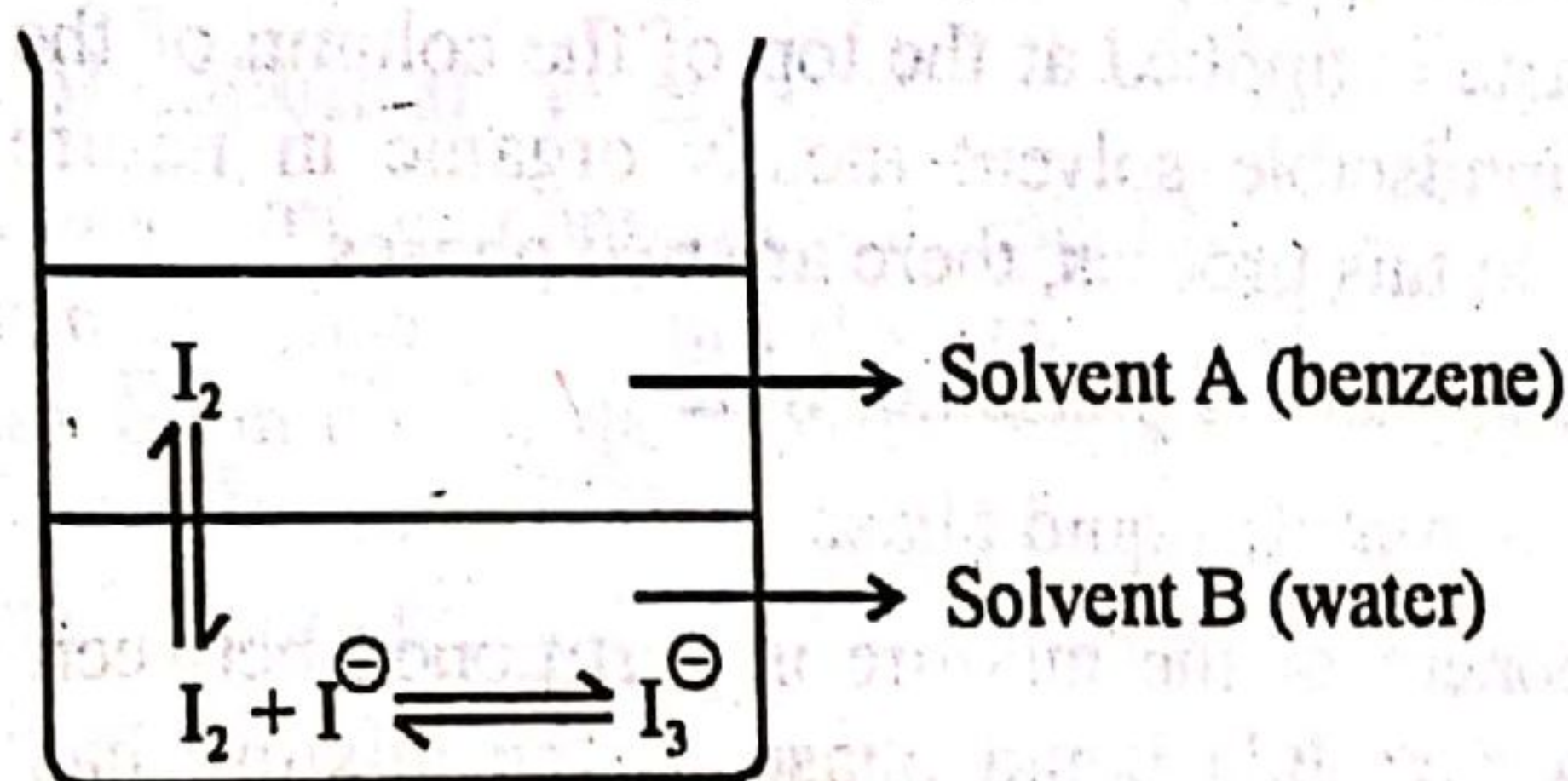

Fig. (28) Distribution of I_2 in water and benzene.

When the system is allowed to stand, the mixture separates into two layers and equilibrium is established.

(i)   The concentration of iodine in two layers i.e. water and benzene is determined by titration by using standard $Na_2S_2O_3$.

(ii) Suppose the concentration of iodine in benzene layer is 'b'.

(iii) Also suppose that the concentration of iodine in water in the form of free iodine 'I' and '$I_3^{\ominus}$' ion is 'c'.
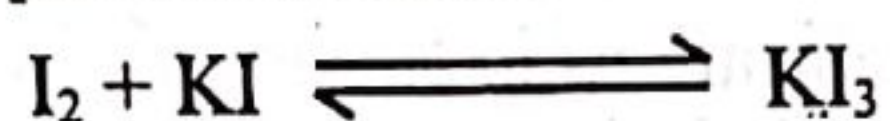
We know that,

$$K_D = \frac{\text{concentration of } I_2 \text{ in water (a)}}{\text{concentration of } I_2 \text{ in benzene (b)}}$$

Concentration of free iodine in water layer $= I_F$

Concentration of KI_3 in water layer $= c - I_F$

Concentration of KI in water layer $= a - (c - I_F)$

The equilibrium constant of following chemical reaction can be written as

$$I_2 + KI \rightleftharpoons KI_3$$

$$K_C = \frac{[KI_3]}{[KI][I_2]}$$

$$K_C = \frac{c - I_F}{(a - c + I_F) \times I_F}$$

If we know all the quantities of on the R.H.S. of this equation, then K_C can be calculated.

(7)   Distribution indicator:

Iodine is least soluble in H_2O. If it is present in H_2O, then its existence and quantity can not be easily judged. For this purpose, we can add a few drops of an organic solvent, say chloroform or CCl_4 in the sample of water having iodine. The bulk of the iodine present in H_2O passes into the organic layer and gives intense violet colour to it. So, the distribution of iodine to greater extent in organic layer indicates itself.

(8)   Partition chromatography:

Partition chromatography is a modern technique in which small amounts of the organic materials are separated from each other. For this purpose, a paste is prepared. This paste is applied at the top of the column of the silica and soaked in water. Another immiscible solvent mostly organic in nature is allowed to flow down the column. In this process, there are two phases,

(i)   Stationary liquid phase i.e. water

(ii) Organic mobile liquid phase.

Each component of the mixture is partitioned between the stationary liquid phase like H_2O and mobile liquid phase. If the mixture has various components then they are separated in the order of distribution co-efficients. That component

which has highest distribution co-efficient is first to move down when the organic phase moves. In this way, it can be collected separately. That component which has lower distribution co-efficient takes more time to come down and it can be collected in another receiver.

(9) Desilverization of Lead:

Let us have molten lead containing silver. Molten zinc is added to this. Zinc and lead form the immiscible layers and silver gets distributed in these two layers. Silver distributes 300 times greater in zinc at 800°C. It means that most of the silver leaves lead. When the zinc layer is cooled, then we get the alloy of silver and zinc.

The alloy of zinc and silver is distilled in a retort. Zinc passes over, leaving silver behind.

That amount of silver, which is still present in lead is recovered with molten zinc in the second installment and so on.

8.11.0 COLLOIDAL SOLUTIONS

8.11.1 Introduction:

In 1861, Thomas Graham noted that the crystalline substances like sugar, glucose, urea and sodium chloride when dissolved in water can pass through a semipermeable membrane. He also observed that the particles of glue, gelatin and gum arabic do not pass through the semipermeable membrane. He called the first substance as crystalloid and the other substances as colloid. This word is derived from the word "Kolla" means 'glue' and 'cidos' means 'like'. Actually this difference is due to the sizes of the particles.

Colloidal solutions are also called colloidal dispersions and their sizes are intermediate between true solutions and suspensions. The diameters of the colloidal particles in the solution lie in the range of 10 A° and 2000 A°. Colloidal solution is also called colloidal dispersion or simply colloid.

Any material in the particle size lying in the colloidal range is said to be in colloidal state.

8.11.2 Shapes of colloidal particles:

The colloidal particles may be rod like, disc like, thin films or long filaments. We can say that a system whose one dimension length, width or thickness lies in the range of 10 – 200 A° is called colloidal dispersion.

8.11.3 Types of colloidal systems:

Colloidal solution is consisted of colloidal particles called the dispersed phase. The phase in which they are dispersed is called dispersion mediam. Both these phases may be in one of the physical states i.e. gas, liquid or solid. So, there are eight types of colloidal solutions. Anyhow, the colloidal dispersion in one gas into another gas is not possible. The colloidal solutions prepared in water as dispersion media are called hydrosols or aquasoles. In case of alcohol and benzene, they are called alcosoles and benzosoles.

A colloidal solution can be simply called as sol.

Types of sols:

Sols can be divided into two classes:

(i)   Lyophilic sols

(ii)   Lyophobic sols

"Lophilic means solvent loving. These are those sols in which the dispersed phase shows a definite affinity for the medium or the solvent." Starch, gum and protein in water are some of the good examples of lypohilic soles.

"Lyopbobic means solvent hating. These are those sols in which the dispersed phase has no attraction for the medium or the solvent." The dispersion of gold, $Fe(OH)_3$ and sulphur in water are good examples of lyopbobic sols.

The forces of attractions in lyophilic sols are mostly due to hydrogen bonding.

8.11.4 Important features of lyophilic and lyophobic sols:

(1)   Lyophilic sols can be obtained easily by mixing certain materials like starch or protein with suitable solvents.

Lyophobic sols can not be prepared so easily.

(2)   Hydrophilic sols may have little or no charge at all while the particles of hydrophobic sols carry positive or negative charge.

(3)   There happens solvation of the colloidal particles in hydrophilic sols, but not in hydrophobic.

(4)   The viscosity of lyophilic soles are usually greater than the pure dispersion medium. But in the case of hydrophobic sols the viscosities do not change.

(5)   Lyophilic sols can be precipitated only by high concentration of electrolytes but lyophobic sols are precipitated with low concentration.

(6)   Lyophilic sols are reversible but lyophobic are irreversible.

(7)   Lyophilic sols do not give tyndall effect, but lyophobic sols do give.

(8)   When electrical field is applied, then lyophilic sols show little tendency to move towards the electrodes, but lyophobic sols show greater tendency to do so.

8.12.0 PREPARATION OF SOLS

Lyophilic sols, for example, soaps, detergents, geltin, gum arabic, and starch can be prepared by simply dissolving these substances in water.

Lyophobic sols are prepared by two types of methods:

(i)   Condensation methods

(ii)   Dispersion methods.

8.12.1 Condensation methods:

In these methods, the ions and molecules which are originally present in the true solutions are converted to insoluble particles of colloidal dimensions by means of chemical reactions.

These methods are as follows:

(i) Reduction:

With the help of this technique, we prepare the colloidal solutions of metals. Preparation of colloidal gold or silver by the reduction of the dilute solution of a salt of the metal is done with the help of a organic reducing agent.

Gold chloride can be reduced with tannin. Silver sol is prepared by reduction of silver carbonate with tannic acid.

(ii) Oxidation:

Colloidal sulphur can be prepared by the oxidation of H_2S. For this purpose, the solutions of H_2S and SO_2 are prepared. The two solutions are mixed with each other in stoichiometric amounts.

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

(iii) Double decomposition:

The colloidal arsenic sulphide can be prepared by the action of H_2S on As_2O_3.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$
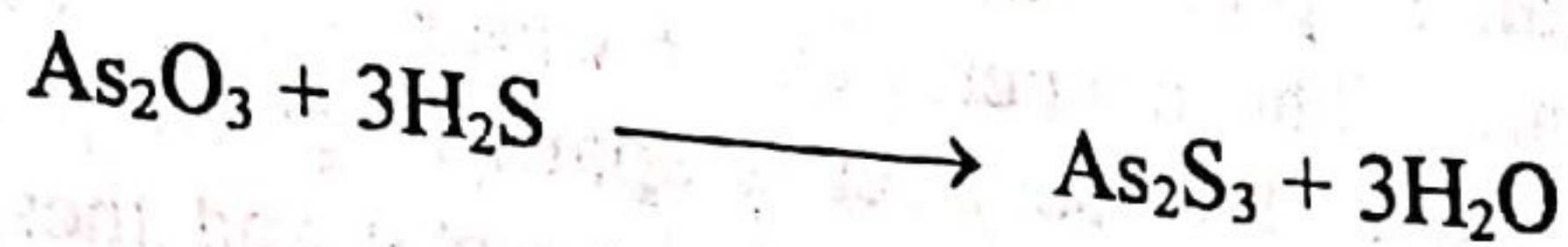
(iv) Hydrolysis:

We can prepare the sol of $Fe(OH)_3$ by the addition of a few cm^3 of conc. $FeCl_3$ with 500 cm^3 of boiling water with constant stirring. Hydrolysis takes place immediately and a beautiful deep red sol of $Fe(OH)_3$ is obtained.

(v) Exchange of solvents:

This is an interesting method to prepare a sol. According to the general principle, if a substance 'A' is soluble 'B', but 'A' is not soluble in 'C', then 'A' will form a colloidal solution when excess of 'C' is added to the original solution of 'A' and 'B'. Remember that 'B' and 'C' should be miscible with each other. In this way, sulphur sol can be prepared by adding a saturated alcoholic solution of sulhur to water.

8.12.2 Dispersion methods:

In these methods, the material in the bulk is dispersed in another medium. We will discuss three methods in this respect.

  (i) Mechanical dispersion

  (ii) Bredig's arc method

  (iii) Peptization

(i) Mechanical dispersion:

A coarse suspension of the substance is prepared in the dispersion medium and is passed through the colloidal mill. The mill is consisted of two steel plates which rotate at very high speed i.e. 7000 rotation per minute in opposite directions.

The particles of the coarse suspension pass through these plates and they face powerful shearing force. In this way, the particles are broken and a sol is prepared. Colloidal graphite, which is a lubricant and the printing inks can be prepared by this method. Following diagram (29) makes the idea clear.
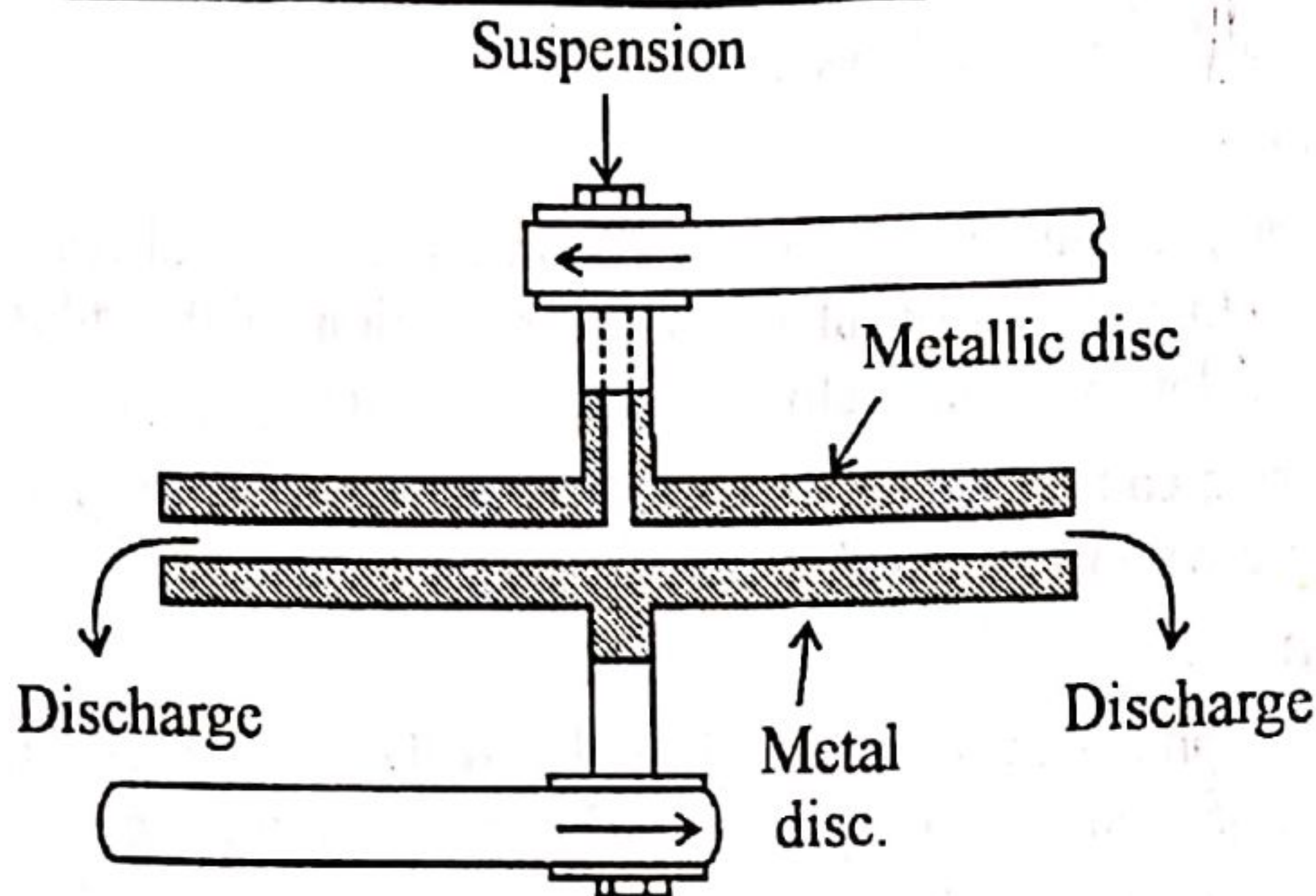
Fig. (29) Disc mill to prepare a colloidal solution.

(ii)   Bredig's arc method:

This is a sort of electrodispersion, and the hydrosols of the metals like that of Ag, Au and Pt, can be prepared. Two metal electrodes are held close together beneath deionized water. The temperature of water is kept very low and a small amount of KOH is added. Intense electric spark is given. Intense heat of spark between the electrodes vapourises some of the metal and these vapours condense under water. These atoms of the metal present in the vapours aggregate to form the colloidal particles. Following diagram (30) makes the idea clear.
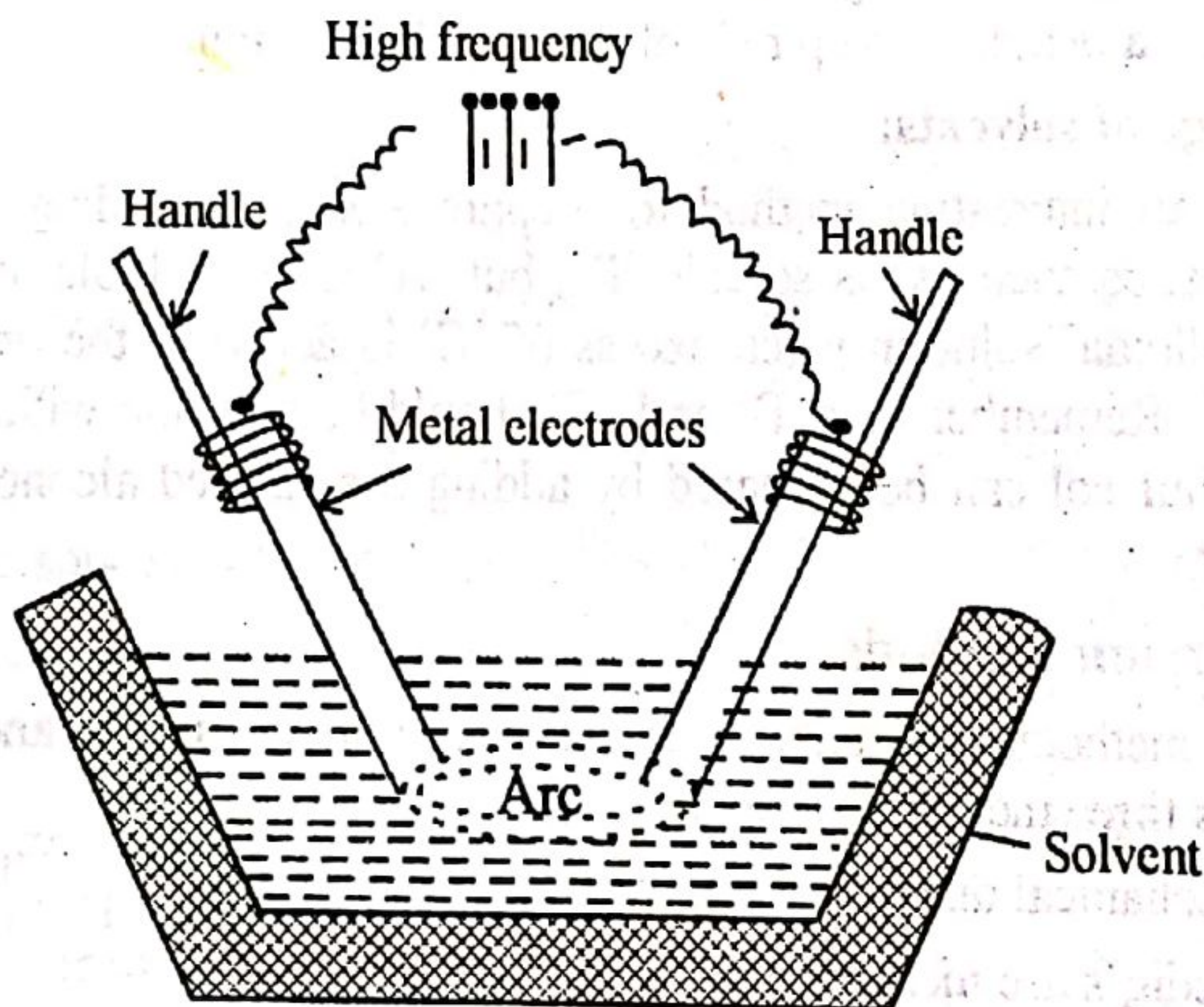

Fig. (30) Bredig's arc method

(iii)   Peptization:

Peptization is the reverse process of coagulation. It is a direct distintegration or dispersion of a substance into particles of colloidal size by using peptizing agent.

Most of the hydrophilic substances such as glue, gum and gelatin are peptized by water. Water acts as a peptizing agents.

AgCl can be converted into sol by adding HCl. Similarly, $Fe(OH)_3$ can give a sol by adding Fe^{+3} ion.

8.12.3 Purification of sols:

Whenever the sols are prepared, then some ionic or molecular substances are also present. In order to purify the sols, these electrolytes have to be removed. Mostly there are following three methods for this purpose:

(i) Dialysis

(ii) Electrodialysis

(iii) Ultrafilteration

(i) Dialysis:

As we have stated earlier that the particles of the two solutions can pass through the membrane but colloidal particles are retained. Colloidal particles diffuse very slowly due to their large sizes. The important membrane used for this purpose may be parchment paper, cellophane, cellulose nitrate and cellulose acetate.

The arrangement is consisted of cylindrical vessel whose one end is covered with the membrane and other is open for the addition of colloidal solution. This cylindrical vessel along with the colloidal solution is placed in a large dish, containing distilled water. The supply of the distilled water is continued. Following diagram (31) shows this arrangement. The particles of the true solution go to the large dish in distilled water. The diagram is shown below to understand the process. Fig. (31)
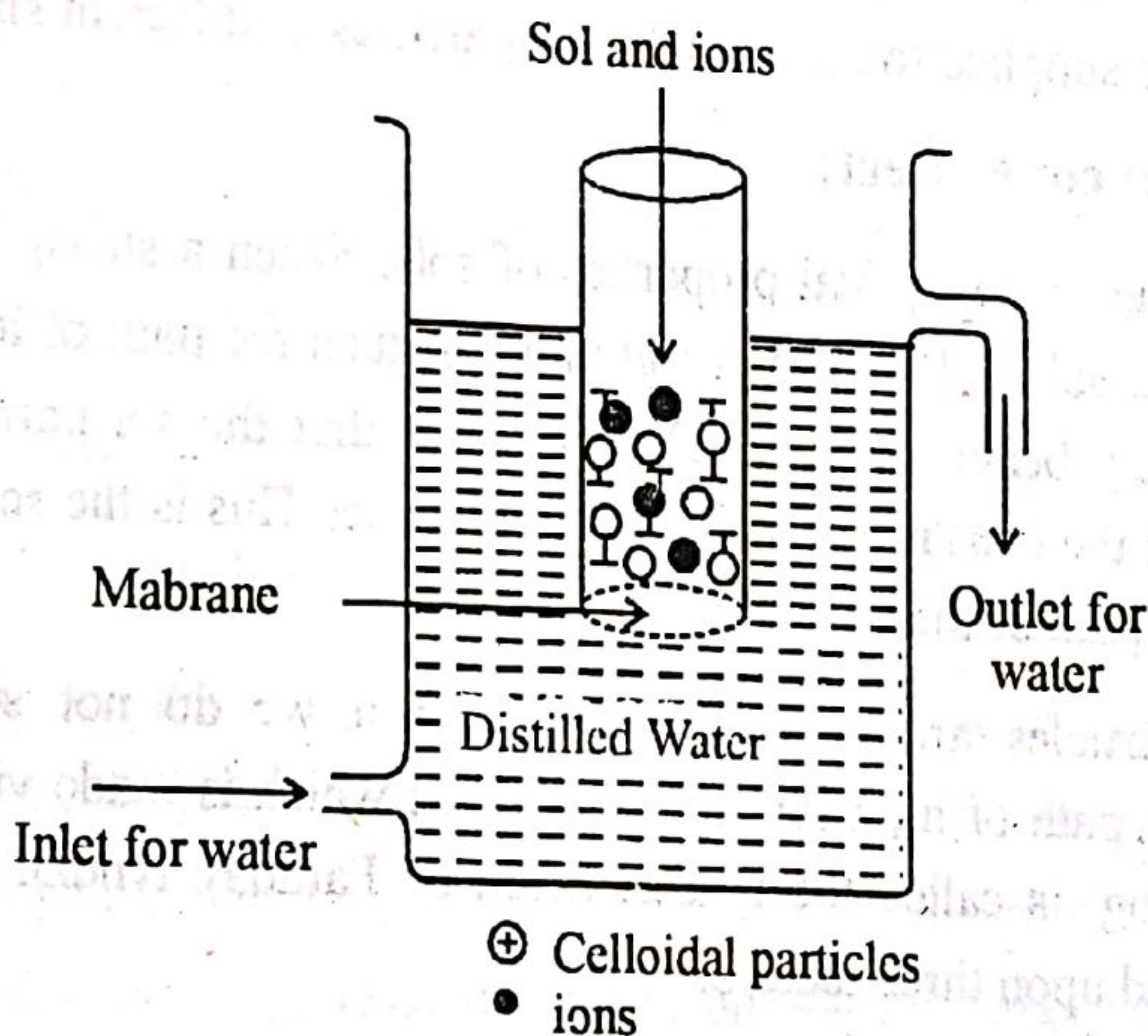

Sol and ions

Mabrane

Outlet for water

Distilled Water

Inlet for water

⊕ Celloidal particles
● ions

Fig. (31) Working of a Dialyser.

(ii) Electrodialysis:

In this method, the dialysis is carried out under the influence of electrical field. The two ends of the dialyser are covered with the membrane. The colloidal solution is placed in drum shaped vessel which is suspended in distilled water. Two electrodes are supplied as shown. The ions of the electrolytes move towards the oppositely charged electrodes. In this way, they are taken away by distilled water. Anyhow, the non-electrolytic impurity like urea and sugar are not removed. Following arrangement (32) makes the idea clear.
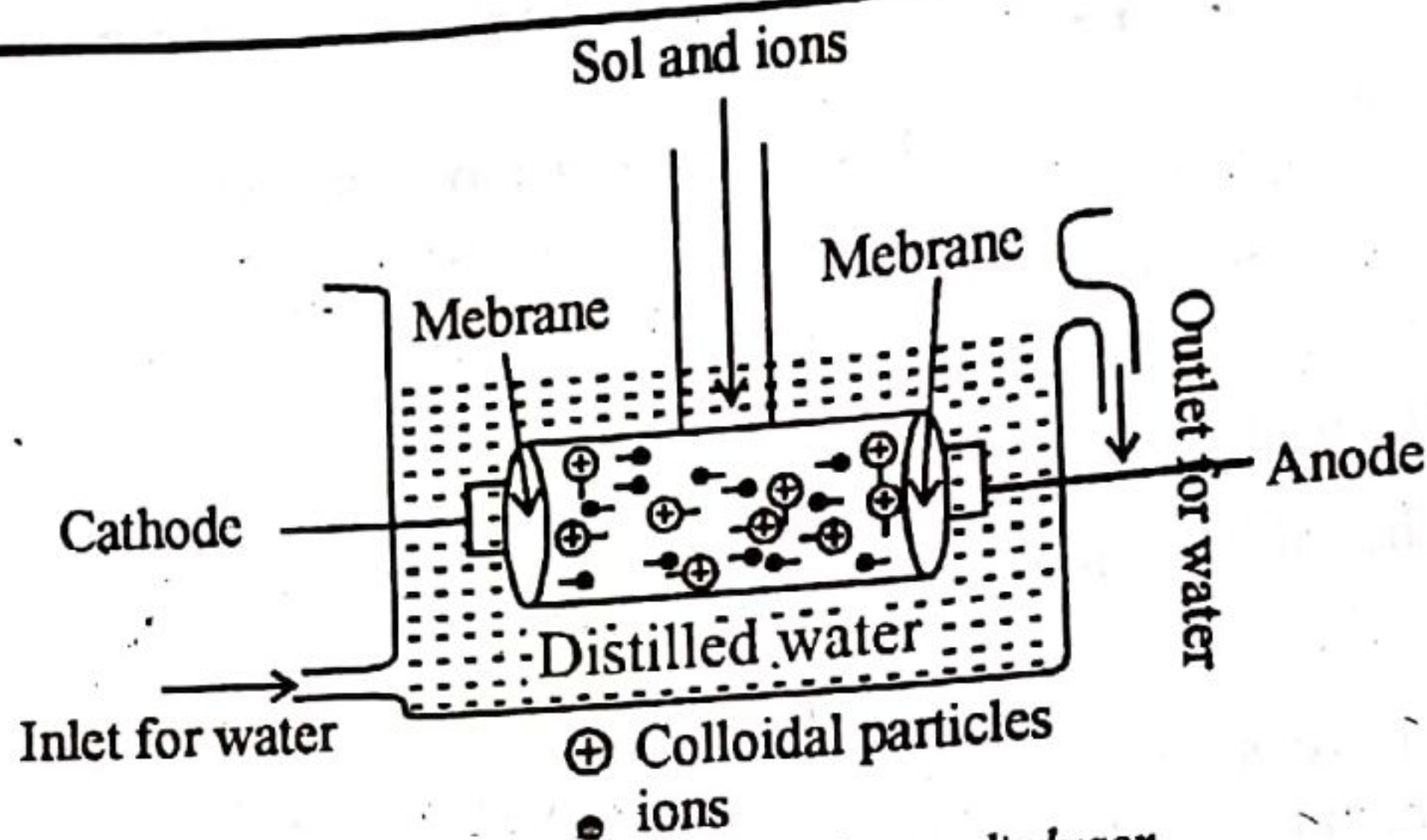
Fig. (32) Working of a electrodialyser

(iii) Ultrafilteration:

It is a separation of sol particles from the liquid medium and electrolytes by filteration through an ultrafilter.

We know that the sol passes through an ordinary paper due to the big sizes of the pores of the filter paper. But, if the filter paper is impregnated with colloid ion or a regenerated cellulose, then the pore sizes of the filter papers are much reduced. This type of modified filter paper is called an ultrafilter. Ultrafiteration is a slow process. If we use the graded ultrafilters, then the technique of ultra filteration can be supplied to separate the sol particles of different sizes.

8.12.4 Tyndall cone effect:

This is one of the optical properties of sols. When a strong beam of light is passed through a sol, and viewed at right angles, then the path of light shows up in the form of hazzy beam, or cone. The reason is that the sol particles absorb the light energy and the emit it in all directions in space. This is the scattering of light. It illuminate the path of the beam.

If the particles are of colloidal size, then we do not see the particles themselves. The path of light through the colloid which is made visible as a result of light scattering, is called the tyndall beam or Faraday tyndall cone. This light scattering depend upon three factors.

(i) Wavelength of the light used

(ii) Difference in the refractive index between the particles and the surrounding medium.

(iii) Size and configuration of the particles.

True solutions donot show the tyndall effect. However, this effect can be observed when the light has to pass through the solutions of particles of very small size having a thick layer of molecules. Diagram (33) shows tyndall cone effect.
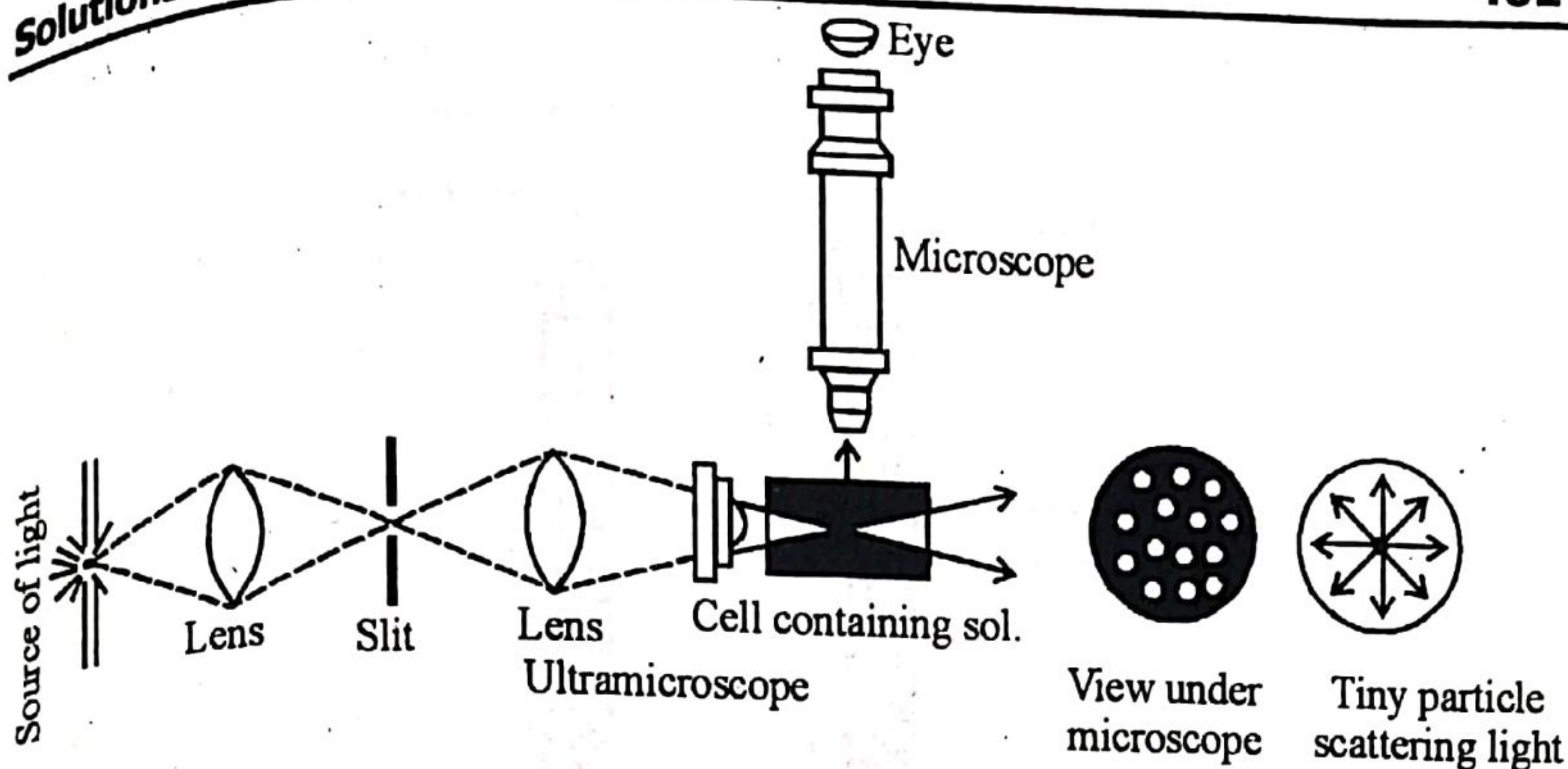
Fig. (33) The diagram of the slit ultramicroscope and Tyndall cone effect.

8.12.5 Applications of Tyndall cone effect:

The blue of the sky and the red of the sunset is a sort of Tyndall cone effect. Actually, the small sized particles of oxygen and nitrogen scatter the shorter wavelength more effectively than longer wavelengths. If there were no scattering, the light would reach us only by direct transmission from the sun or by reflection from the surfaces. Hence, the sky would appear as dark in day time as at night, and the sun would act as a huge spot of light during the day.

8.12.6 Electrophoresis:

It is a movement of electrically charged colloidal particles under the influence of applied electrical field.

In order to study the electrophoretic effect, we consider the following arrangement Fig. (34). It is a U-shaped tube fitted with a stop cock for drainage. The funnel shaped filling tube is attached. First of all some quantity of distilled water is placed in a tube. Then the sol is introduced through the funnel. In this way, water is displaced upwards. Sharp boundaries are produced in the two arms. Electrodes are introduced in the two side arms and connected to a source of potential. If the colloidal particles are positively charged, the level of the sol falls gradually on the anode side, and rises on cathode side.

During the process of electrophensis, the sol particles reach the respective electrodes and after getting discharged, they are precipitated. The phenomenon of electrophosis is explained in the Fig. (34).
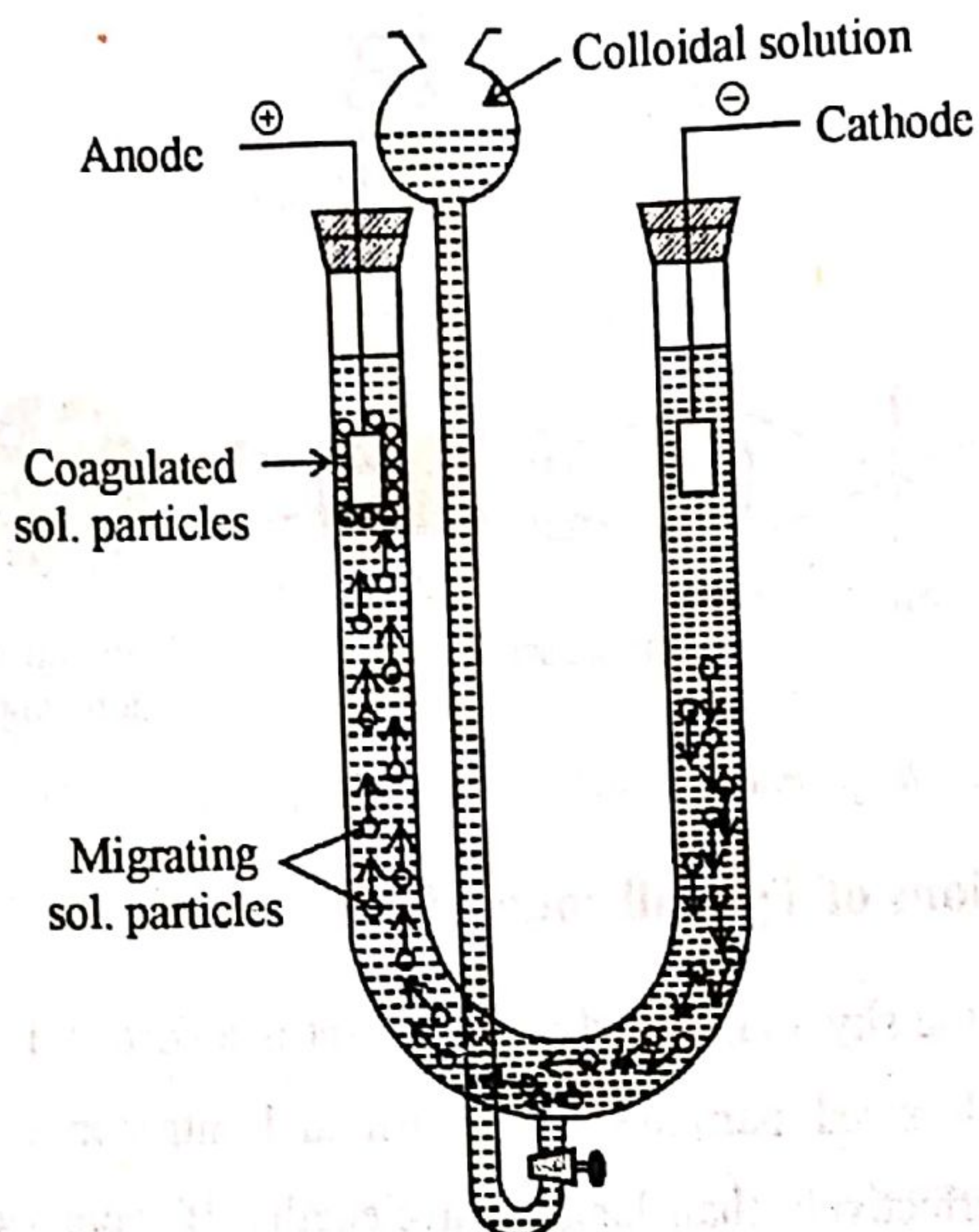
Fig. (34) Electrophoresis

The phenomenon of electrophoresis can be used to determine the sign of the charge on the colloidal particles. We can also measure the rate of traveling of colloidal particles. Since, different colloidal species in a mixture travel at different rates, so separation can be performed by this method. *So electrophoresis is used extensively for the fractionation and analysis of proteins, nucleic acids, polysacchrides and other complex substances of biological interests.*

8.12.7 Electro-osmosis

This process is just the reverse of electrophoresis. In this process, the liquid moves through a fixed porous material.

Following arrangement Fig. (35) can help us to understand the process. A U-shaped tube is fitted with a porous material 'M'. This porous material may be wool or a porous clay diaphragm. The electrical current is set up across the electrode. The dispersion medium moves towards the other electrode. This phenomenon of electro-osmosis is used technically in the removal of water from moist clay and for drying the pastes. Look at of the following diagram (35) to understand it.
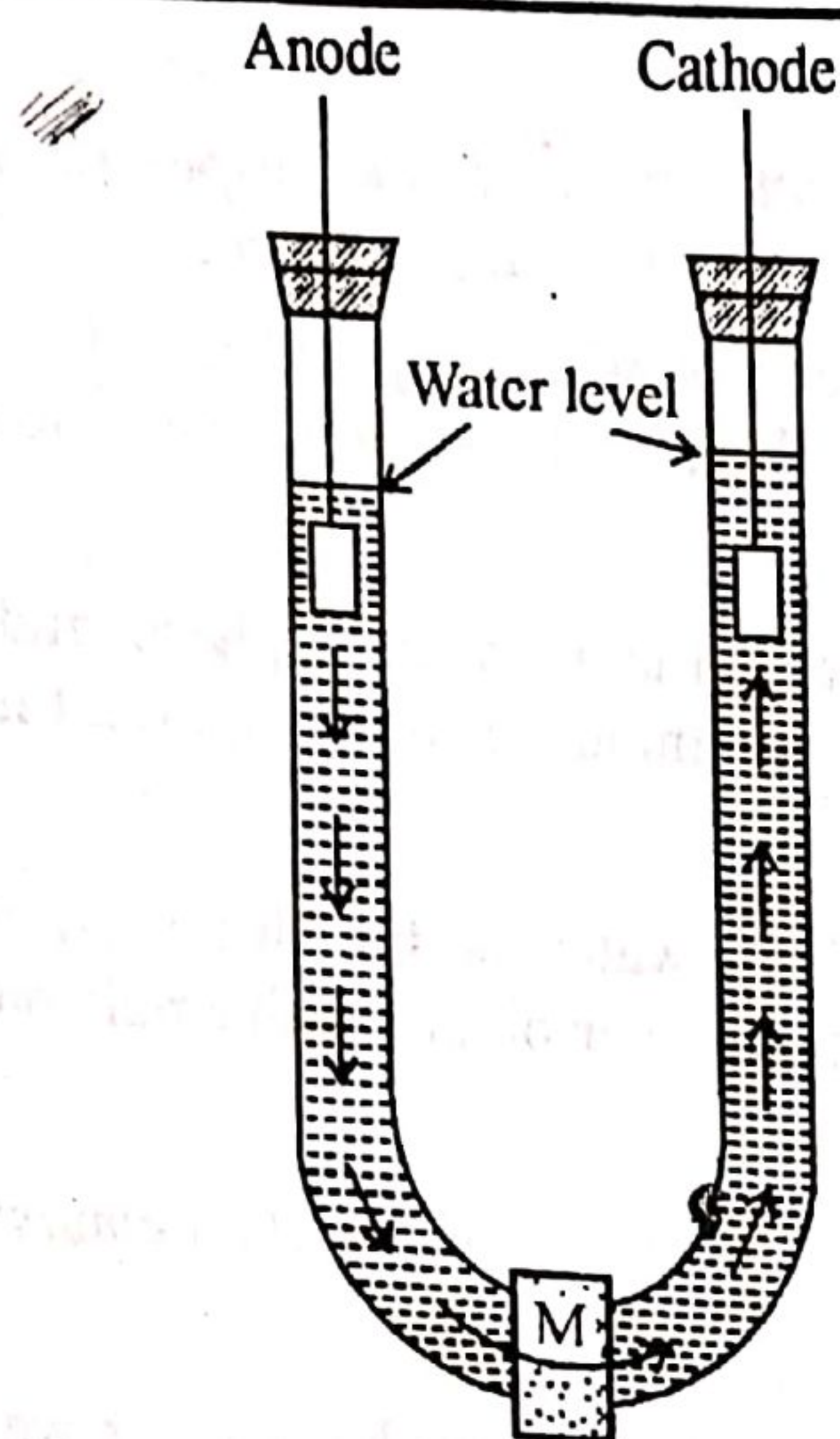
Fig. (35) Arrangement for electro-osmosis.

8.12.8 Streaming Potential:

The phenomenon of streaming potential can be studied from the same above mentioned diagram for electro-osmosis. In this arrangement the electrodes of the apparatus are not connected to the battery but to a galvanometer. Initially, there will be no current. But if water is forced through the tube, than electromotive force is indicated in a galvanometer. It can be noted very easily that the potential which is produced is proportional to the pressure. The potential so developed is called streaming potential.

8.12.9 Sedimentation Potential or Dorn effect:

The word sedimentation means settling down. This phenomenon can be observed, if the particles are forced to move in a resting liquid. This can be done by gravitational force. The potential so produced is known as sedimentation potential. This is also called "Dorn effect".

This process is just the reverse of electrophoresis.

8.13.0 MACROMOLECULES

There are certain substances which are themselves composed of giant molecules and dissolve in a solvent to give colloidal solution directly. Such giant molecules are called macromolecules. The dimensions of the macromolecule lie in the range of 10 – 1000 A°. The best examples are gelatin, synthetic polymer, synthetic rubbers, cellulose and starch. The solutions of macromolecules behave like a reversible colloid and are lyphilic sols. They have high viscosities and show a weak tyndall effect. Anyhow, they donot carry an electrical charge and donot show electrophoresis.

8.13.1 Emulsion:

"Those colloidal solutions in which the dispersed phase as well as the dispersion medium are liquids are known as emulsions."

Depending upon the fact that which type of liquid is dispersion phase and the other is dispersion medium, there are two types of emulsions.

(i)   Oil in water emulsion:

Those emulsions in which oil is a dispersed phase, and water is a dispersion medium. **Milk** is one of the best examples in which liquid fat is dispersed in water.

(ii)   Water in oil emulsion:

Those emulsions in which water is the dispersed phase and oil is the dispersion medium. **Butter** and **cod liver** oil are such emulsions.

8.13.2 Emulsification:

"The process of producing an emulsion is called emulsification."

Preparation of emulsion:

Two immiscible liquids are shaken together e.g., if we shake oil or benzene with water the oily liquid can be dispersed in droplets but emulsion is not stable. The droplets quickly recombine and the two liquids separate into two layers. In order to stabilize the emulsion, an emulsifying agent is added.

Emulsifying agent helps the formation of droplets by lowering the interfacial tension. It prevents them from coagulating. The function of emulsifiers is to act as a protective layer around the oil droplets of emulsion. In this way, its stability increases.

Most commonly used emulsifying agents are **soaps** and **detergents**. Some other stabilizing agents are **proteins** and **gums**. Digestion of fats in the intestines is facilitated by emulsification. A small amount of fat forms Na-soap with the alkaline solution of intestine. It emulsifies the rest of the fat and makes it easier for the digestive enzymes to do their work.

Many lotions, creams and ointments are emulsions of oil in water and of water in oil type. Emulsions find applications in the concentrations of ores as well.

8.13.3 Distinction between "oil in water" and "water in oil" emulsion:

Following two tests are applied to distinguish between two types of emulsions.

1.   Dye test:

If the emulsion is heated with the oil soluble dye and emulsion gains the colour of the dye, then it is water in oil emulsion. If the emulsion does not catch the colour of the dye, then it will be oil in water emulsion.

2.   Conductance method:

Add a small amount of electrolyte in emulsion. If the conductance increases, the emulsion is "oil in water" type and if there is no appreciable change in conductance, then it is "water in oil" type emulsion.

8.13.4 Structure of emulsion particles:

Emulsion is produced by mixing two immiscible liquids and an emulsifying agent. The emulsifying agent is 0.5 to 5 %. In order to understand it, let us consider an emulsion in which soap is used as an emulsifier in "oil in water" emulsion. The hydrocarbon part of soap molecule will be attracted by the oil and the polar heads will be directed into water as shown in Fig. (36).

In this way, the droplets of oil will be protected from coalescence by a protective layer of emulsifier. The droplets whose surfaces are covered with soap molecules are however electrically charged by the ionized carboxylic group of the soap. In this way droplets of oil repel each other before they collide and so the emulsion is stabilized.

8.13.5 Factors for the stability of emulsion:

Stability of emulsion depends on following factors:
(i) Thickness of the protective film.
(ii) Compactness of the protective film.
(iii) Electrical charge on the droplet or the film.
(iv) Viscosity of dispersed medium.
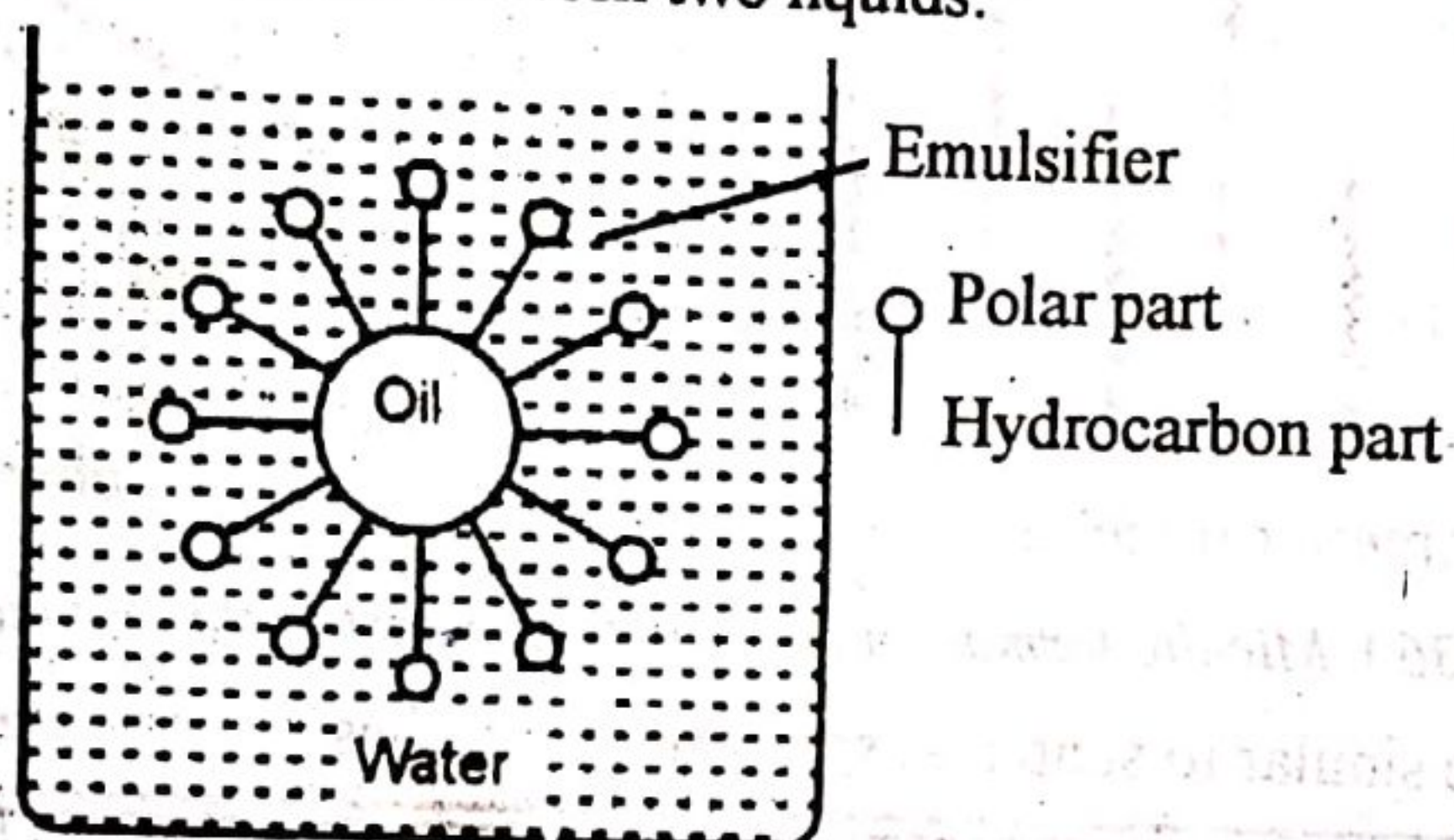(v) Density difference between two liquids.

Fig. (36) Role of emulsifier

8.13.6 Demulsification:

The process of breaking emulsion to yield the constituent liquids is called demulsification.

Following techniques can be used:
(i) Heating
(ii) Centrifuging
(iii) Adding large amount of electrolytes to precipitate out the dispersed phase. Separation of cream from milk is an example of demulsification by means of centrifugation.

8.14.0 MISCELLES

Certain strong electrolytes give a normal solution at low concentration but show colloidal nature at high concentration. These substances may also be called miscelles or they may be referred as associated colloids.

Soap is one of the best examples of miscelle. Actually such substances are surface active. They consists of lyophilic as well as lyophobic parts in the same molecule. Soap is the Na or K salt of long chain carboxylic acids. The long hydrocarbon chain acts as a lyophobic while the ionic group which is carboxylic in nature serves as lyophilic. Miscelle may contain as many as hundreds of molecules.

In miscelle formation, hydrocarbon chains point to the center, leaving the polar carboxylic group on the outer surface as shown in the following diagram (36). This polar outer surface is in contact with water. This miscelle is solvated by large number of water molecules. The miscelle has usually size of colloidal particle. Since it is charged, so it is a colloidal ion and the parent substance is the colloidal electrolyte. Miscelle attracts a large number of Na and K ions all over its surface.
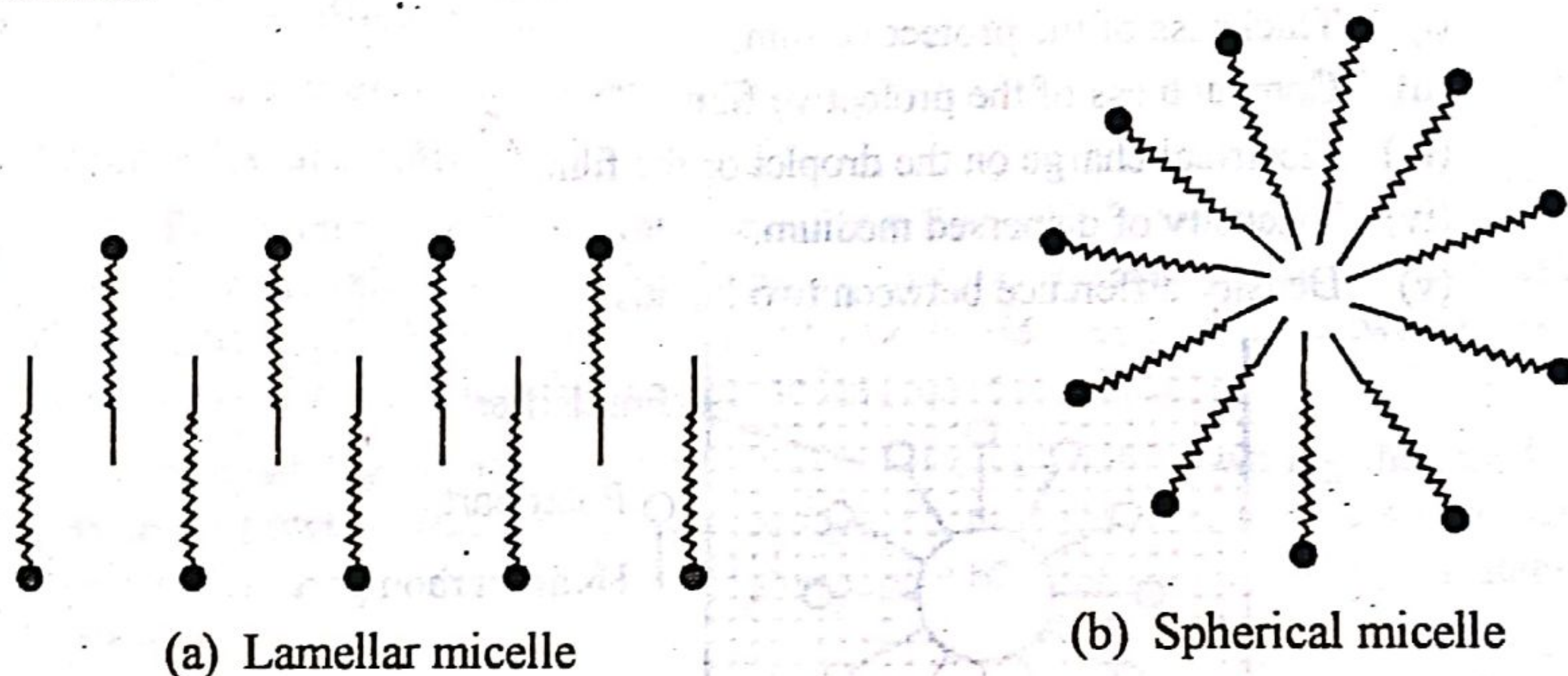

(a) Lamellar micelle   (b) Spherical micelle

Fig. (36) Micelle formation (They actually exist in three dimensions)

Detergents are similar to soap and so form the micelles.

8.15.0 GELS AND JELLIES

"Jellie is a common name for gel and they are semi-rigid sols consisting of two components in which one is a solid and other is a liquid."

Table jellies are prepared from gelatin. Fruit jellies like jams contain the so called pectins. Pectins are soluble gum like carbohydrates.

8.15.1 Classification of gels:

Gels may be classified as:
(i) Elastic gels.
(ii) Rigid or non-elastic gels.
(iii) Thioxotropic gels.

The best examples of elastic gels are those which are produced from sols of gelatin, agar, starch, jams, jellies and many kinds of puddings.

Silica gel is a non-elastic gel. Many of the metallic hydroxides and hydrated metal oxides are non-elastic gels.

Reversible isothermal sol gel transformation is found in certain sols such as colloidal iron oxide and aluminium. If these are allowed to stand undisturbed, then gel formation takes place and if the resulting gel is shaken sol is reformed. This reversible sol gel transformation is known as thioxotropy. This is very important in paints.

8.16.0 IMPORTANCE OF COLLOIDS

Many of the substances can exist in colloidal state. All the fields of chemistry are related with colloidal chemistry by one way or the other:

1. All living tissues are colloidal in nature so the complex chemical reactions which are necessary to life must be interpreted in terms of colloidal chemistry.

2. The phenomenon of adsorption, dialysis and coagulation are important in preparative chemistry and analytical chemistry e.g. co-precipitation, washing of precipitate, filtration and chromatographic analysis are studied in analytical chemistry.

3. Colloidal science is important in manufacture of paints, plastics, textiles, photographic paper and films, glues, inks, cements, ceramics, rubber, leather, lubricants, soaps and synthetic detergent.

4. Items like agricultural sprays, insecticides, aerosols, gels and jellies, butter, cheese, salad and adhesives involve the colloidal chemistry.

5. Some important processes like printing, bleaching, decolorizing, tanning, dying and the separation of pulverized ores involve the colloidal chemical aspect. Colloidal chemistry finds important applications to biology and medicine e.g. blood and protoplasm are complex colloidal solutions. Skin, muscles and many different tissues are gels with peculiar structure.

6. The coagulation of colloidal solutions is a very important phenomenon. This fact is applied in nature to a number of technical problems which are as follows.

(i) **Purification of drinking water:**

Ordinary water contains suspended impurities. The particles of impurities are of colloidal size, and they don't settle down due to similar charges on them. When potash alum is added, then Al^{+3} ions neutralize the charge on colloidal particle. In this way, they settle down and the water becomes fit for drinking.

(ii) **Medicines:**

Many medicines are being produced in the form of soles. Such medicines are more affective because they have greater assimilation and adsorption qualities.

(iii) **Pollution control:**

Smoke is a colloidal solution of carbon particles in air. Carbon particles can be coagulated by using the conductor near the exist of chimney. In this way, carbon particles settle down and the carbonless fumes or air comes out of chimneys. This design is known as Cottrell dust precipitation.

(iv)   Photography:

The photographic film contains the colloidal solution of silver bromide in gelatin. This film can be obtained on a glass plate by depositing a mixture of silver bromide and gelatin.

(v)   Sewage disposal:

The sewage disposal carries dirt particles suspended in water. Sewage water is allowed to come in contact with an electrode of opposite charge in a big tank. In this way, dust particles are precipitated and separated. These particles can act as manure.

(vi)   Tanning:

Both hides and skins are gel structure containing proteins in the colloidal form. We can tan hides to leather by using common salt. Anyhow, in general practice, the precipitation is done by means of alum, chromium salt or by tans from bark of trees.

(vii)   Curd formation:

When milk sours, then bacteria form lactic acid form milk sugar. This acid changes the colloidal casein into curd.

(viii)   Delta formation:

Delta is formed at a place where the river enters the sea. Actually, sea water is rich in minerals, while river contains colloidal particles of clay. When the two waters meet then clay is coagulated. This clay is fertile and is known as delta.

(ix)   Natural rubber:

Natural rubber is obtained from secretion of certain trees as an emulsion of negatively charged particles in water called latex. This latex is changed into rubber by means of dilute acetic acid or by smoke. It is slightly acidic.

(x)   Blue colour of sky:

Colloidal particles of dust in atmosphere only scatter blue light and absorb rest of the light. Hence blue light reaches us and sky seems to be blue.

(xi)   Chemical warfare:

Smoke and mist screens are formed by the explosion of bombs. They are harmful to humans. So we have to wear the gas masks. These masks contain colloidal charcoal, so the dangerous smoke and mist particles are precipitated down and the human life is saved.