

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 (وہ صفات جو سالموں کے اکٹھے پر منحصر ہوں). These are the properties of solutions and not of the pure substances.

There are four colligative properties:

- (1) Lowering of vapour pressure (بخارات کے دباؤ کا کم ہونا)
- (2) Elevation of boiling point (B.P. کا بڑھنا)
- (3) Depression of freezing point (F.P. کا کم ہونا)
- (4) Osmotic pressure. (نفوذی دباؤ)

Actually, all the colligative properties are developed (پیدا ہوتی ہیں) due to the lowering of vapour pressure. All these properties are obeyed (مانی جاتی ہیں), when the following conditions are satisfied:

- (i) Solution is dilute (ارٹکاز کم ہو)
- (ii) Solute is non-volatile (آسانی سے بخارات نہ بننے والا)
- (iii) Solute is non-electrolyte (نا برق یا شئی)

یاد رکھیں بخارات کے دباؤ کا گرتا colligative property ہے۔ کسی سویوٹنر کے بخارات کی قیمت کالی گیسو پراپرٹی نہیں ہے۔ اس طرح B.P. میں اضافہ (ΔT_b) اور F.P. میں کمی (ΔT_f) دونوں کالیکنٹو صفات ہیں۔ نہ کہ صرف B.P. اور F.P. ان صفات کے زمرے میں آتی ہیں۔

Now, let us discuss these properties one by one

8.5.1 Lowering in Vapour Pressure:

We have already mentioned different statements (بیانات) of Raoult's law. When a non-volatile (بخارات میں جلدی نہ بدلنے والا), non-electrolyte (بجلی کی روکوند گزرنے دینے والا) solute is dissolved in volatile solvent then according to Raoult's law, the relative lowering of vapour pressure (V.P. کی مقابلیت) is equal to mole fraction of the solute

$$\frac{\Delta P}{P^\circ} = X_2 \quad \dots\dots (1)$$

- ΔP = Lowering of vapour pressing
 P° = 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 X_1 and that of solute is X_2 .

Since,
$$X_2 = \frac{n_2}{n_1 + n_2} \quad \dots\dots (2)$$

So,
$$\frac{\Delta P}{P^\circ} = \frac{n_2}{n_1 + n_2} \quad \dots\dots (3)$$

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

Hence,
$$n_1 = \frac{W_1}{M_1} = \frac{\text{Mass of solvent}}{\text{Molar mass of solvent}}$$

$$n_2 = \frac{W_2}{M_2} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}}$$

So,
$$\frac{\Delta P}{P^\circ} = \frac{W_2/M_2}{W_2/M_2 + W_1/M_1} \quad \dots\dots (4)$$

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

$$\frac{\Delta P}{P^0} = \frac{W_2/M_2}{W_1/M_1}$$

$$\boxed{\frac{\Delta P}{P^0} = \frac{W_2 \times M_1}{M_2 \times W_1}} \quad \dots\dots (5)$$

مساوات (5) ہم نے n_2 کو نظر انداز کر کے بنائی ہے۔ اصل میں یہ کالی گیٹو صفات صرف کم سے کم ارتکاز والے سویوشنز پر پوری اتنا ہی یعنی 0.1 مولیلیٹی یا اس سے بھی کم ہے۔ لہذا اگر n_2 کی قیمت 0.1 بھی ہے۔ اور سالونٹ اس سے 500 گنا سے بھی زیادہ ہے تو 0.1 کو نظر انداز کیا جاسکتا ہے۔
With the help of this equation (5), we can calculate molar mass ' M_2 ' of the solute which is non-volatile and non-electrolyte.

15.2 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 solutions are non-volatile and non-electrolyte. From the given 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

solute. 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 (ΔP). Hence, we prove that lowering of vapour pressure is a colligative property. In other words lowering of vapour pressure (ΔP) is independent of the nature of solute the weather it is urea, glucose or

Solution Solvent Weighed CaCl₂ Tubes
Fig. (8.12) Walker's and Ostwald's method for measuring the lowering of vapour pressure.

8.6.0 ELEVATION IN BOILING POINTS (نقطہ جوش میں افراز) (Ebullioscopy) (نقطہ جوش کی پیمائش)

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 (افراز بڑھنا) 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 (8.13). 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.

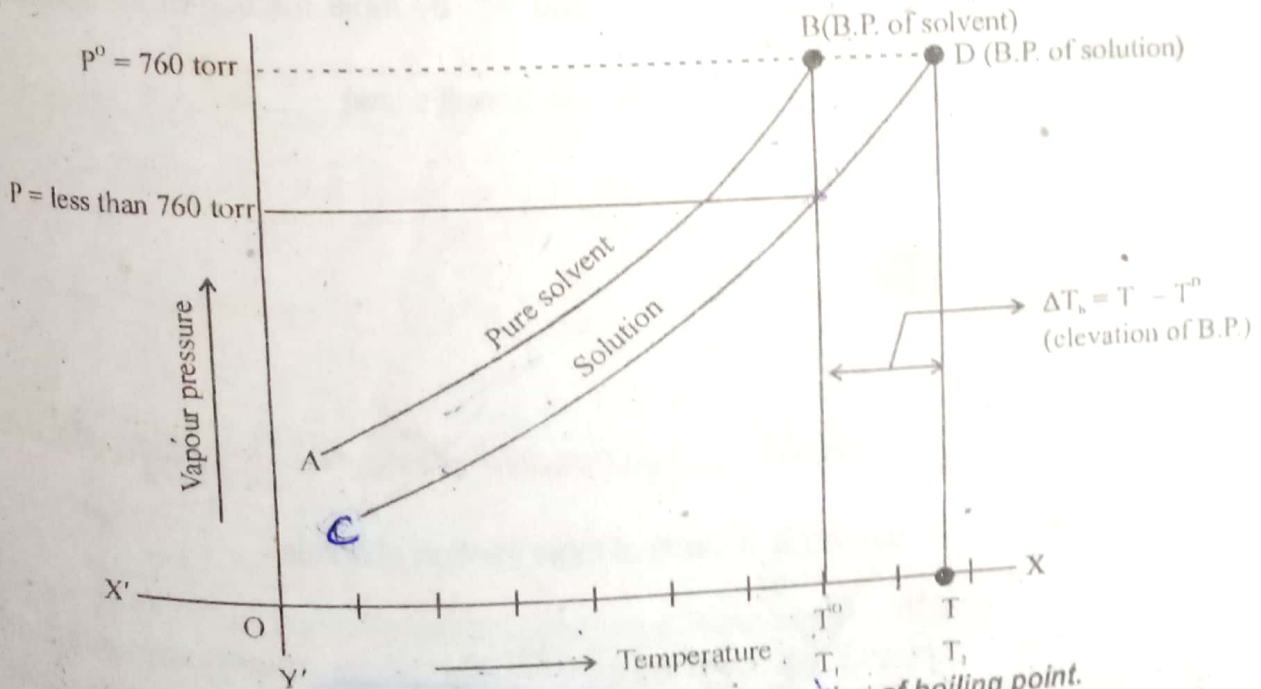


Fig. (8.13) Graphical representation of elevation of boiling point.
 Pure solvent boils at T° , when the external pressure is P° . Solution will boil at the external pressure 'P', with temperature 'T'. Hence ΔT_b is the elevation of boiling point.
 $P =$ Vapour pressure of solution at the boiling point of pure solvent

Mathematical treatment:

In chemical thermodynamics (کیمیائی حرکیات), there is well known mathematical relation known as Clausius - Clapeyron equation,

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

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 whose base is e). If we apply this equation to the above graph, then we can say that,

$$\ln \frac{P^0}{P} = \frac{\Delta H_v}{R} \left[\frac{T - T^0}{T T^0} \right] \quad \dots\dots (2)$$

(ΔH_v وہ حرارت ہے جو ایک مول مائع کے B.P پر پوری طرح بخارات میں تبدیلی کے لئے درکار ہے۔)

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, i.e., inverting the P and P⁰, and putting $T - T^0 = \Delta T_b$

$$-\ln \frac{P}{P^0} = \frac{\Delta H_v}{R} \left[\frac{\Delta T_b}{T T^0} \right]$$

Since, the solution is dilute,

Hence, $T \approx T^0$

(جب سولیوشن کا ارتکاز بہت ہی کم ہو تو B.P میں اضافہ اتنا کم ہوتا ہے کہ ہم آسانی سے یہ کہہ سکتے ہیں کہ T اور T⁰ برابر ہیں۔ یہ مساوات کو درست کرنے کے لئے حربہ استعمال کیا جاتا ہے۔)

So, $T T^0 \approx T^0^2$

$$-\ln \frac{P}{P^0} = \frac{\Delta H_v}{R} \left[\frac{\Delta T_b}{T^0^2} \right] \quad \dots\dots (3)$$

Now, let us substitute the vapour pressure 'P' and 'P⁰' by mole fraction of the solution. This can be done by applying the Raoult's law.

Since, $P = P^0 X_1$ (according to Raoult's law)

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

As, $X_1 + X_2 = 1$

So, $X_1 = 1 - X_2$

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

(یعنی $\frac{P}{P^0}$ کے جگہ سولیوشن کا مول فریکشن لکھ دیا ہے۔ اس تبدیلی کے لئے Raoult کے قانون کا سہارا لیا ہے۔)

Putting values of $\frac{P}{P^0}$ in equation (3) in terms of mole fraction of solute

$$-\ln (1 - X_2) = \frac{\Delta H_v}{R} \cdot \frac{\Delta T_b}{T^0^2} \quad \dots\dots (4)$$

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

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

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

Hence, $\ln(1 - X_2) \approx -X_2$ (5)

(اگر X_2 کی قیمت فرض کیا $0.001 = X_2^2$ تو $0.00001 = X_2^3$ ہے۔ اور X_2^3 اس سے بھی چھوٹی ہے۔ لہذا X_2^2 , X_2^3 وغیرہ کو نظر انداز کیا جاسکتا ہے۔)

Put equation (5) in (4)

$$-(-X_2) = \frac{\Delta H_v}{R} \cdot \frac{\Delta T_b}{T^{\circ 2}}$$

$$X_2 = \frac{\Delta H_v}{R} \cdot \frac{\Delta T_b}{T^{\circ 2}} \quad \text{..... (6)}$$

This equation (6), can be rearranged

$$\Delta T_b = \frac{RT^{\circ 2}}{\Delta H_v} X_2 \quad \text{..... (7)}$$

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, $\frac{R(T^{\circ 2})}{\Delta H_v}$ is a collection of constant quantities, so, we can say that ' ΔT_b ' is proportional to

$$\Delta T_b \propto X_2$$

$$\text{Since, } X_2 = \frac{n_2}{n_1 + n_2}$$

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

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

$$m = \frac{n_2}{\text{solvent in kg}}$$

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,

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

جس وقت بھی کسی کیمیائی مرکب کا ایک مول 1000 گرام پانی میں حل کیا جائے تو ایک مولل سولوشن تیار ہوتا ہے۔ لیکن اگر 0.1m ہو تو ہم نے 0.1 کو نظر انداز کر بھی دیں تو X_2 کی قیمت کو کوئی فرق نہیں پڑتا۔ کیونکہ $n_2 = 0.1$ اور 1000 گرام سالونٹ فرض کیا جائے اس کے جو مولز بنتے ہیں وہ n_1 ہیں۔ $n_1 = \frac{1000}{18} = 56$ لہذا $X_2 = \frac{0.1}{56 + 0.1}$ یا $X_2 = \frac{0.1}{56}$ ایک ہی بات ہے۔ ہم نیچے سے 0.1 کو نظر انداز کر رہے ہیں۔ اس حالت میں سولوشن 0.1 مولل کہلائے گا۔ لہذا n_2 کی قیمت مولیلیٹی کے برابر ہے۔۔

Putting this value of ' X_2 ' in the above equation (7)

$$\Delta T_b = \left[\frac{RT^{\circ 2}}{\Delta H_v n_1} \right] m \quad \text{..... (8)}$$

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. It means $T^{\circ 2}$, ΔH_v and n_1 are properties of solvents and they are all constants.

All the quantities in the brackets give another constant called K_b

$$K_b = \frac{RT^{\circ 2}}{\Delta H_v n_1} \quad \text{..... (9)}$$

یہاں ہمیں یہ پتہ چلا کہ کسی سالونٹ کی K_b کی قیمت کن صفات پر انحصار کرتی ہے۔ یعنی T° اور ΔH_v اور n_1 ۔

$\therefore K_b$ 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 $\Delta T_b = K_b \cdot m$ (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 (فیصلے جو دلیل پر مبنی ہوں) 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 (مشاہدہ کیا جانا تجربے سے) and calculated (حساب لگانا مساوات سے) value of K_b should agree with each other.

3.6.2 Calculation of Molar Masses From Elevation of Boiling Points:

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

$$\text{Molality (m)} = \frac{\text{Mass of the solute (W}_2\text{)}}{\text{Molar mass of the solute (M}_2\text{)}} \times \frac{1}{\text{Mass of the solvent in kg. } \left(\frac{W_1}{1000}\right)}$$

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

$$m = \frac{1000 W_2}{M_2 \cdot W_1} \text{ (11)}$$

Substituting equation (11) in (10)

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

Rearranging

or $M_2 = \frac{K_b}{\Delta T_b} \left(\frac{1000 W_2}{W_1} \right)$ (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 solvent. The solution should be dilute to obey this equation.

8.7.0 DEPRESSION IN FREEZING POINT (نقطہ انجماد میں کمی)

(CRYOSCOPY) (نقطہ انجماد کی پیمائش)

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 (صاف سالونٹ کے مقابلہ میں سو لیشن کا نقطہ انجماد کم ہوتا ہے). This is again due to the lowering of vapour pressure of solution.

8.7.1 Graphical representation:

In order to have a through (مکمل) 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 'T°' is the freezing point of pure solvent (خالص سالونٹ کا نقطہ انجماد) corresponding to the point 'B'. If the solvent is cooled further, the 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 (عمل تسعید کا خم دار خط) the solvent. At the freezing point of the pure solvent "T_f^o" the solid and the liquid phases are in equilibrium and the solvent in the both phases has same vapour pressure "P^o".

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. (8.16)

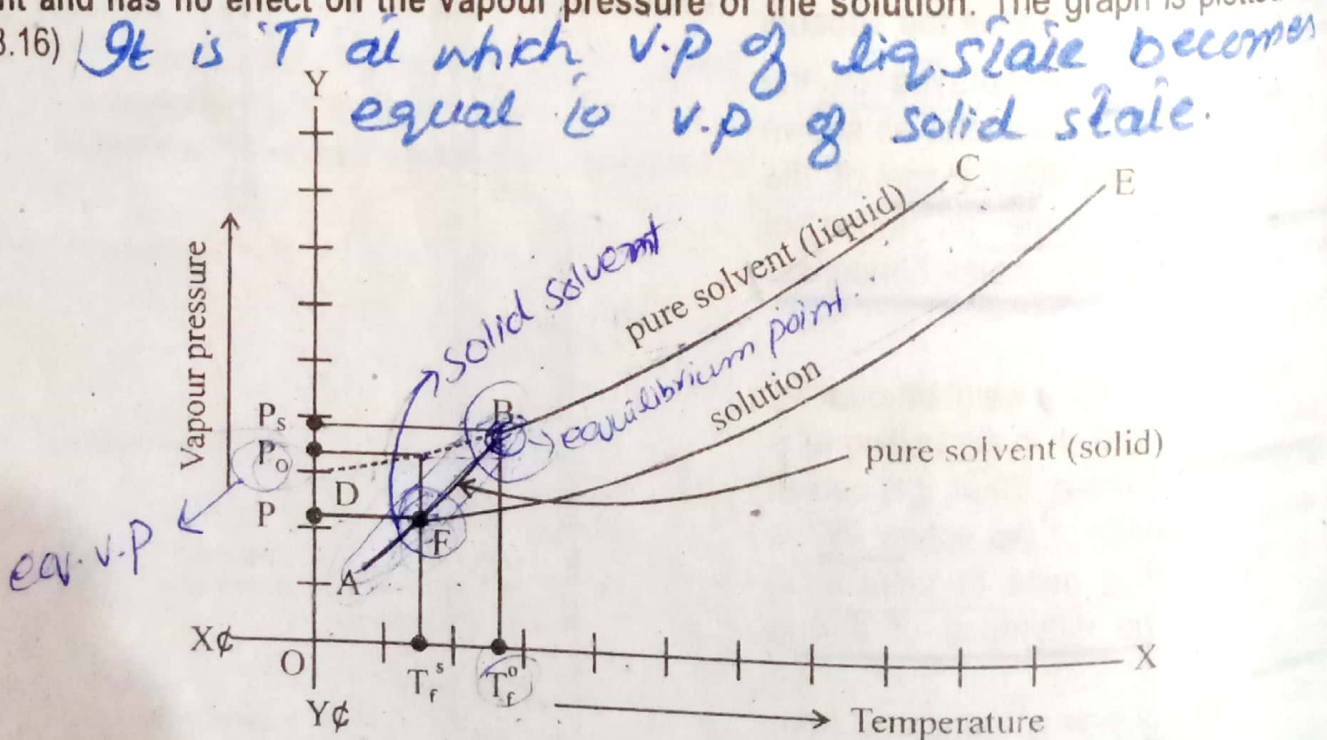


Fig. (8.16) Study of Depression of F.P. of a solution.

The depression of freezing point is

$$\Delta T_f = T_f^o - T_f^s$$

Mathematical Explanation:

We take the help of Clausius - Clapeyron equation, which relates (تعلق قائم کرتی ہے) 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 '
 P^o = V.P. of pure super cooled liquid at ' T_f^s '

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

In order to apply Clausius - Clapeyron equation, we have the following proposal (پیشورہ):

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

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

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

$$\Delta H_s - \Delta H_v = \Delta H_f \dots \dots (2)$$

Here, ΔH_s = Heat of sublimation (ایک مول مرکب کا پوری طرح ٹھوس سے بخارات میں تبدیل کرنے کے لئے درکار توانائی)

of the solid solvent

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

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

$$\begin{aligned} & \ln \frac{P_s}{P^o} - \ln \frac{P_s}{P} \\ &= \ln \frac{P_s}{P^o} - \ln \frac{P_s}{P} - (\ln \frac{P_s}{P} - \ln P) \\ &= \ln \frac{P_s}{P^o} - \ln P - \ln \frac{P_s}{P} + \ln P \\ &= \frac{\ln P}{P^o} \end{aligned}$$

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

$$\Delta H_s - \Delta H_v = \Delta H_f \text{ (Heat of fusion)}$$

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 fractions of the components. According to first definition of Raoult's law

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

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

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

The equation (3) is converted into,

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

During the expansion of the L.H.S.

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

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

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

Since, $T_f^o - T_f^s = \Delta T_f$
 $T_f^o T_f^s = T_f^{o2}$ (solution is very dilute)

Hence, $X_2 = \frac{\Delta H_f}{R} \cdot \frac{\Delta T_f}{T_f^{o2}}$

Rearranging (منظم سے ترتیب دینا) the above equation

$$\Delta T_f = \left[\frac{RT_f^{o2}}{\Delta H_f} \right] X_2 \dots\dots (5)$$

Since $X_2 = \frac{n_2}{n_1 + n_2}$ and the solution is dilute, 'n₂' 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 'n₁' becomes the molality of solution. Equation (5) becomes,

$$\Delta T_f = \left[\frac{RT_f^{o2}}{\Delta H_f \cdot n_1} \right] m \dots\dots (6)$$

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 cryoscopic constant

$$K_f = \frac{RT_f^{o2}}{\Delta H_f \cdot n_1} \dots\dots (7)$$

(K_f کی قیمت T_f^o, ΔH_f اور n₁ پر انحصار کرتی ہے۔)

Hence, equation (6) can be written as

$$\Delta T_f = K_f \times m \dots\dots (8)$$

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'

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

← $\frac{W_2}{M_2} \times \frac{1000}{W_1}$

Hence equation (8) becomes,

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

Rearranging this equation

$$M_2 = \frac{K_f}{\Delta T_f} \times \left(\frac{1000 W_2}{W_1} \right) \dots\dots (9)$$

If we know the 'K_f' value of the solvent Table (8.4), depression of freezing point (نقطہ انجماد میں کمی) 'ΔT_f', weight of the solute 'W₂' and weight of the solvent 'W₁', then we can calculate the molar mass of non-volatile, non-electrolyte solute.

8.8.0 OSMOSIS

When a solution is separated from its solvents by a semipermeable membrane (پوری دار جھلی) then the solvent flows to the solution side through the membrane.

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

8.8.1 What is Semipermeable Membrane:

A semipermeable membrane is a thin layer (پتی تہہ) which permits the passage of one type of molecules, generally the solvents.

Examples:

- (i) Parchment (جھلی)
- (ii) Fish bladder (مچھلی کا مثانہ)
- (iii) Lining of egg shell (انڈے کی سفیدی کی جھلی)
- (iv) Cellophane (کاغذ سے مشابہ بہت باریک اور شفاف پلاسٹک کا تجارتی نام)

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

8.8.2 Experimental Study of Osmosis: Omp

Nollet was the person who did first experiment on osmosis (نفوذ پذیری) in 1748. A simple arrangement is that a piece of parchment is tightly stretched (گس کے باندھا ہوا) across the belly (پیت) of a thistle funnel as shown in the following diagram. Fig. (8.18)

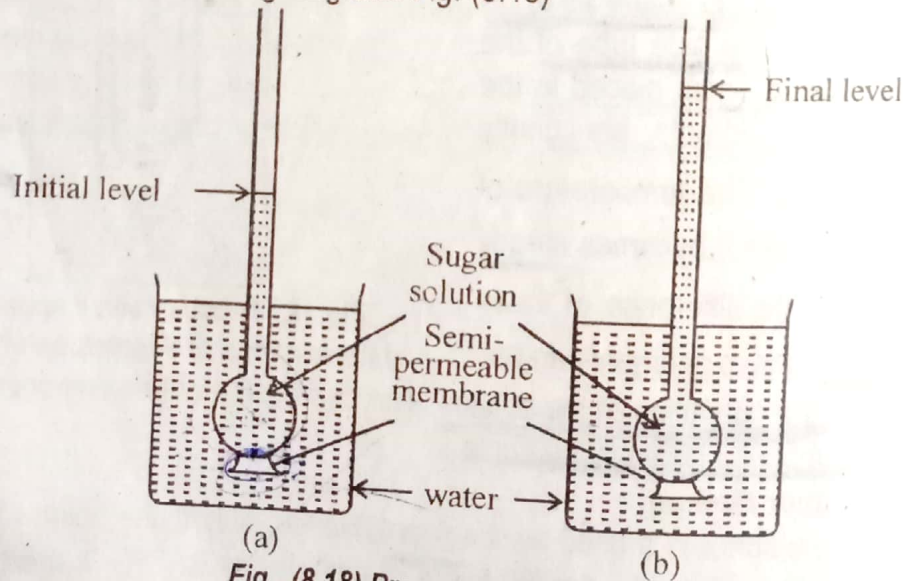


Fig. (8.18) Process of osmosis.

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 solvent molecules bombard (ٹکریں مارتے ہیں) the membrane and set up a pressure (ایک دباؤ پیدا کرتے ہیں). 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 (پانی کا دباؤ) 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."