Colligative properties:

Colligative properties are those which depend entirely upon the number of particles of the solute contained in a known amount of the given solvent and not at all upon the nature (i.e. chemical composition or constitution) of the solute. The various colligative properties are —

1. Lowering of vapour pressure.
2. Osmotic pressure.
3. Elevation of boiling point.
4. Depression of freezing point.

Lowering of vapour pressure by a non-volatile solute:

When a non-volatile solute is dissolved in a liquid, the vapour pressure of the solution becomes lower than the vapour pressure of the pure solvent. It is called lowering of vapour pressure by non-volatile solute.

Raoult, in 1887, established a relationship between the lowering of vapour pressure of a solution and the mole fraction of the non-volatile solute.

Let us consider a solution obtained by dissolving n_2 moles of a non-volatile solute in n_1 moles of a volatile solvent.

$\therefore$ Mole fraction of the solvent, $x_1 = \frac{n_1}{n_1+n_2}$.

Mole fraction of the solute, $x_2 = \frac{n_2}{n_1+n_2}$.

$\because$ The solute is non-volatile, its vapour pressure is negligible.

$\therefore$ The vapour pressure of the solution is merely the vapour pressure of the volatile solvent.

According to Raoult's law,

Vapour pressure of the solution, $p_1 = x_1 p_1^\circ \longrightarrow (1)$.

where p_1° is the vapour pressure of the pure solvent.

Lowering of vapour pressure $= p_1^\circ - p_1$.

$\therefore$ Relative lowering of vapour pressure $= \dfrac{p_1^\circ - p_1}{p_1^\circ} \longrightarrow$ (ii)

Putting the value of p_1 from in eqn (ii), we get

Relative lowering of vapour pressure $= \dfrac{p_1^\circ - x_1 p_1^\circ}{p_1^\circ}$

$$= \frac{p_1^\circ (1 - x_1)}{p_1^\circ}$$

$$= (1 - x_1)$$

$$= x_2 \quad [\because x_1 + x_2 = 1] \longrightarrow \text{(iii)}$$

From eqn (iii) it is seen that, the relative lowering of vapour pressure of a solution is equal to the mole fraction of the non-volatile solute present in the solution. Hence it is a colligative property.

Thermodynamic derivation of Relative lowering of vapour pressure:

The addition of a non-volatile solute to a solvent at a given temperature and pressure results in the lowering of vapour pressure of the solvent. As a result, the chemical potential of the solvent is also decreased.

At equilibrium, $d\mu_1^v = d\mu_1^l$

where $d\mu_1^v$ is the change in chemical potential of the solvent vapour.

$d\mu_1^l$ is the change in chemical potential of the liquid solvent.

The chemical potential of the solvent in solution phase depends upon T, P and its mole fraction but in vapour phase it depends only on T, P. Thus

$$\mu_1^l = f(T, P, x_1) \text{ and } \mu_1^v = f(T, P) \longrightarrow \text{(i)}$$

$$\therefore (d\mu_1)^l = \left(\frac{\partial \mu_1}{\partial T}\right)^l_{P, x_1} dT + \left(\frac{\partial \mu_1}{\partial P}\right)^l_{T, x} dP + \left(\frac{\partial \mu}{\partial x_1}\right)^l_{T, P} dx_1 \longrightarrow \text{(ii)}$$

But $\left(\dfrac{\partial \mu_1}{\partial T}\right)^l_{P, x_1} = -\bar{S}_1 \longrightarrow$ (iii)

and $\left(\dfrac{\partial \mu_1}{\partial P}\right)^l_{T, x_1} = \bar{V}_1 \longrightarrow$ (iv)

where, $\bar{V}_1$ and $\bar{S}_1$ are partial molar volume and partial molar entropy of the solvent respectively.

Hence,

$$(d\mu_1)^l = -\bar{S}_1^l dT + \bar{V}_1^l dP + \left(\frac{\partial \mu_1}{\partial x_1}\right)^l_{T,P} dx_1 \longrightarrow (v)$$

For an ideal solution,

$$\mu_1^l = \mu_1^0 + RT\ln x_1 \longrightarrow (vi)$$

$$\therefore \left(\frac{\partial \mu_1}{\partial x_1}\right)^l_{T,P} dx_1 = \frac{RT}{x_1} \longrightarrow (vii)$$

At constant T and P (1 atm let), from eq^{n}s (v) and (vii),

$$(d\mu_1)^l = \frac{RT\, dx_1}{x_1} \longrightarrow (ix)$$

$\because$ At a given temperature, the chemical potential of vapour is affected by a change in pressure, we have

$$(d\mu_1)^v = \left(\frac{\partial \mu_1}{\partial P}\right)_{T,x_1} dP = \bar{V}_1 dP \longrightarrow (x)$$

For an infinitely dilute binary solution, $\bar{V}_1 = V_1$

$$\therefore (d\mu_1)^v = V_1 dP \longrightarrow (xi)$$

assuming that the vapour behaves as an ideal gas,

$$V_1 = \frac{RT}{P_1}$$

$$\therefore \text{Eq}^n (xi) \Rightarrow (d\mu_1)^v = \left(\frac{RT}{P_1}\right) dP \longrightarrow (xii)$$

$\because$ At equilibrium, $(d\mu_1)^v = (d\mu_1)^l$, from eq^{n}s (ix) and (xii).

$$\left(\frac{RT}{P_1}\right) dP = \left(\frac{RT}{x_1}\right) dx_1 \longrightarrow (xiii)$$

$\because x_1 + x_2 = 1$.

$\therefore dx_1 + dx_2 = 0$

$$\Rightarrow dx_1 = -dx_2 \longrightarrow (xiv)$$

$$\therefore \text{Eq}^n (xiii) \Rightarrow \left(\frac{RT}{P_1}\right) dP = -\left[\frac{RT}{(1-x_2)}\right] dx_2 \longrightarrow (xv)$$

$$\Rightarrow \frac{dP}{P_1} = \frac{-dx_2}{(1-x_2)} \longrightarrow (xvi)$$

Integrating eqn (xvi) between limits $x_2 = 0$, $p_1 = p_1^\circ$ and $x_2 = x_2$, $p_1 = p_1$, we get,

$$\int_{p_1^\circ}^{p_1} \frac{dp}{p_1} = -\int_{x_2=0}^{x_2=x_2} \frac{dx_2}{1-x_2}$$

$$\Rightarrow \ln\left(\frac{p_1}{p_1^\circ}\right) = \ln(1-x_2).$$

$$\Rightarrow \frac{p_1}{p_1^\circ} = 1-x_2.$$

$$\Rightarrow \cancel{1-\frac{p_1}{p_1^\circ}}\ 1 - \frac{p_1}{p_1^\circ} = x_2.$$

$$\Rightarrow \frac{p_1^\circ - p_1}{p_1^\circ} = x_2.$$

But $(p_1^\circ - p_1)$ is the vapour pressure lowering and $\left(\frac{p_1^\circ - p_1}{p_1^\circ}\right)$ is the relative ~~lowering~~ vapour pressure lowering. Thus relative lowering of vapour pressure is equal to mole fraction of the solute.

<u>Determination of Molar Mass of a non-volatile solute from vapour pressure lowering :</u>

The mole fraction of the solute is given by,

$$x_2 = \frac{n_2}{n_1 + n_2} \longrightarrow (1)$$

For a dilute solution, $n_2 \ll n_1$.

$$\therefore (1) \Rightarrow x_2 = \frac{n_2}{n_1}$$

$$= \frac{w_2/M_{w_2}}{w_1/M_{w_1}}$$

$$= \frac{w_2 M_{w_1}}{w_1 M_{w_2}}$$

where, w_2 is the amount of the solute dissolved in w_1 amount of the solvent, M_{w_1} is the molar mass of the solvent and M_{w_2} is the molar mass of the solute.

But, according to Raoult's law,

$$x_2 = \frac{p_1^\circ - p_1}{p_1^\circ} \longrightarrow (11)$$

$\therefore$ Eqn (I) and (II)

$$\Rightarrow \frac{p_1^\circ - p_1}{p_1^\circ} = \frac{w_2 M_{w_1}}{w_1 M_{w_2}}$$

$$\Rightarrow \boxed{M_{w_2} = \frac{w_2}{w_1} \frac{M_{w_1} p_1^\circ}{w_1 (p_1^\circ - p_1)}}$$

This can be used to determine the molar mass of a non-volatile solute dissolved in a suitable solvent.

Measurement of vapour pressure lowering:

(1) **Static Method:** In this method the vapour pressure of the solvent is determined by the usual barometric technique and the difference in the vapour pressure of the solvent and the solution is determined with the help of a differential manometer. One arm of the manometer is connected with the solution while the other with the solvent. An oil or any other suitable liquid of low density is used as the manometric liquid. The difference in vapour pressure can thus be read directly from the difference in levels of the liquid in the two limbs.

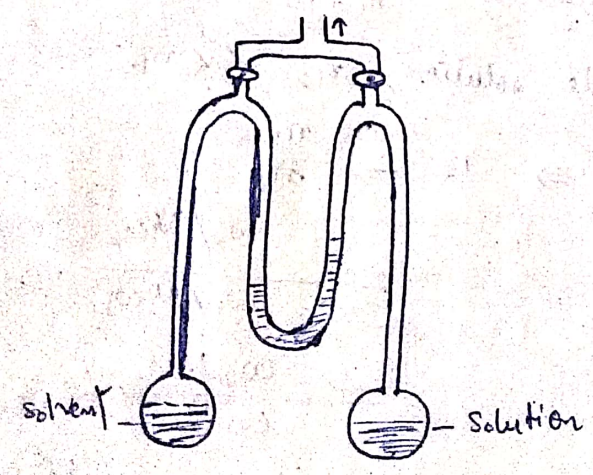


Fig: A differential manometer

(2) Dynamic Method: This method was developed by Ostwald and Walker. In this method, a stream of dry air is bubbled successively through (a) the solution (b) the pure solvent and (c) a reagent which can absorb the vapour of the solvent. As the solvent is usually water, the reagent is generally anhydrous ~~calcium~~ calcium chloride.

The first three bulbs contain a weighed amount of the solution under examination and the next three bulbs contained a weighed amount of the pure solvent. A weighed amount of anhydrous $CaCl_2$ is taken in the set of U-tubes at the end.

All the bulbs are kept at the same temperature and air is bubbled gently to ensure that it ~~goes~~ gets saturated with the vapour in each bulb. The air, as it passes through the solution-bulbs, takes up an amount of vapour which is proportional to the vapour pressure (p) of the solution at the prevailing temp^r. When this moist air passes through the solvent, it takes up a further amount of vapour to get saturated. This amount is proportional to the difference $(p^\circ - p)$ in vapour pressure of the pure solvent and the solution.

Thus, Loss in mass of solution (bulbs) $\propto p$.

Loss in mass of solvent (bulbs) $\propto p^\circ - p$.

$\therefore$ Loss in mass of solution + loss in mass of solvent $\propto (p + p^\circ - p)$.

$\propto p^\circ$.

The calcium chloride tubes are weighed at the end of the experiment. The gain in mass should be equal to the total loss in mass of the solution and solvent which in turn is proportional to p°.

i.e. $$\frac{\text{Loss in mass of solvent (bulbs)}}{\text{Gain in mass of } CaCl_2 \text{ (tubes)}} = \frac{p^\circ - p}{p^\circ}.$$

Thus, knowing the loss in mass of the solvent and gain in the mass of the $CaCl_2$, it is possible to calculate the relative lowering of vapour pressure.

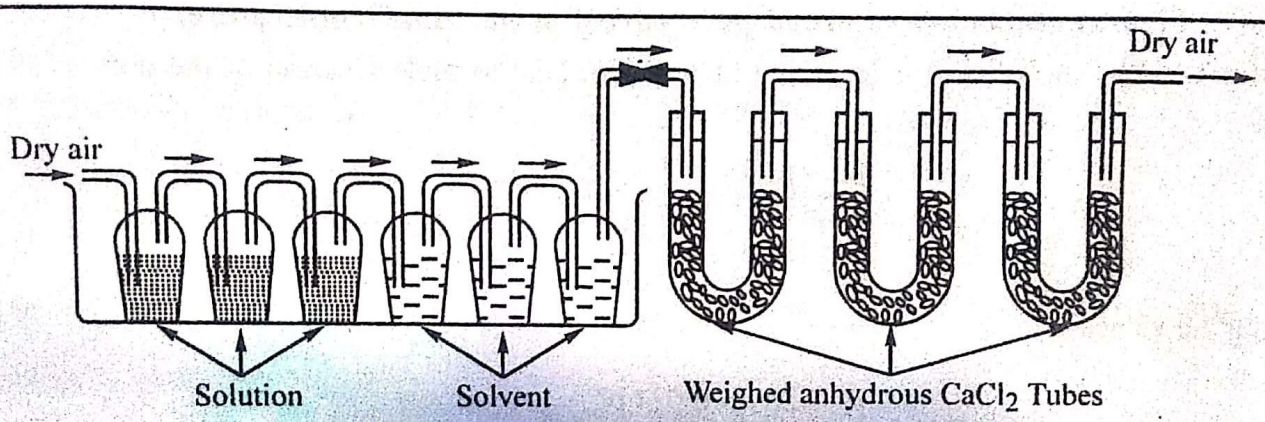


Fig. 2. The Ostwald-Walker apparatus for measurement of lowering of vapour pressure.

Osmosis and osmotic pressure:

The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semipermeable membrane is called osmosis.

The minimum extra pressure that is applied on the solution side and stop the flow of the solvent through a semipermeable membrane is called osmotic pressure.

Measurement of osmotic pressure:

① **The Morse - Frazer Method:** In this method, the solvent is taken in the porous pot, the walls of which contain the semipermeable membrane of copper ferrocyanide. The solution is ~~taken~~ is taken in the bronze cylinder. The glass tube T, open at both ends, serves to keep the pot full with water at atmospheric pressure. The manometer containing air or nitrogen is attached to the outer bronze cylinder B. The solvent tends to pass through the porous pot to the cylinder through the semipermeable membrane. This results in the ~~excess~~ development of excess pressure which is recorded on the manometer. The measured pressure gives the osmotic pressure of the solution. This technique ~~gives~~ enables measurement of osmotic pressure upto 250 atm.

Imp

② **The Berkeley - Hartley Method:** This is the best known method for the measurement of osmotic pressure. Copper ferrocyanide is deposited in the pores of a porcelain tube T. This deposit acts as the semi permeable membrane SPM. This porcelain tube is enclosed in a metallic jacket (J), which is further fitted with a reservoir of pure solvent S at one end and a capillary tube A at the other end. The metallic jacket is fitted with an arrangement for applying external pressure which can be measured with the help of a pressure gauge G.

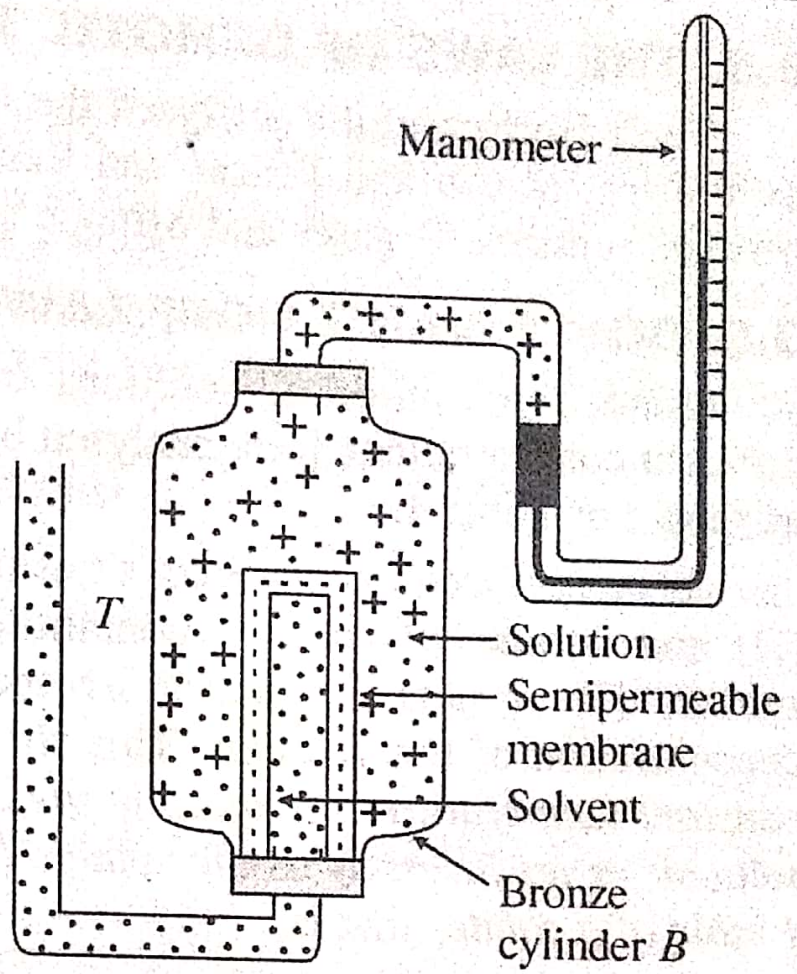


Fig. 4. The Morse-Frazer method for measuring osmotic pressure.

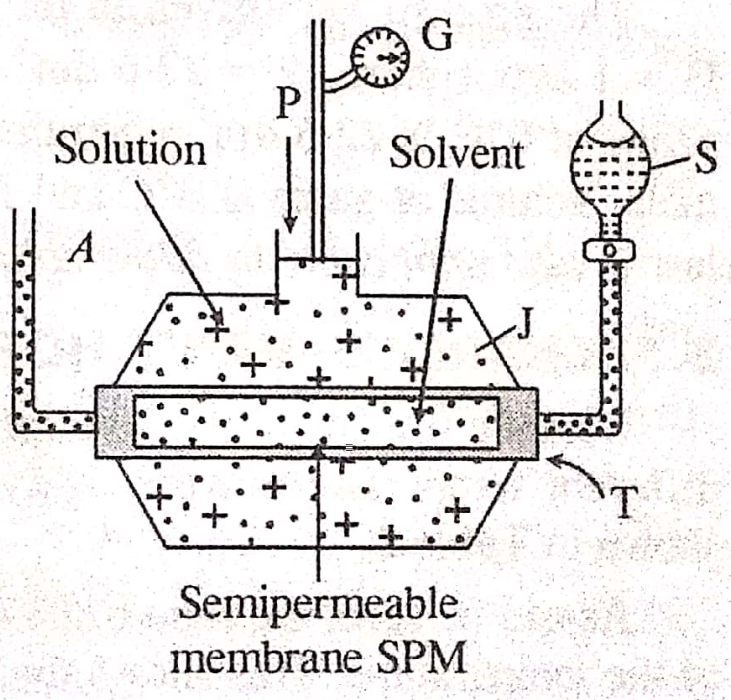


Fig. 5. The Berkeley-Hartley apparatus for measuring osmotic pressure.

The porcelain tube T is filled with the pure solvent and the outer metallic jacket with the solution. Osmosis will start and solvent from the capillary will start moving through the SPM into the solution kept in the jacket. The level of the solvent in the capillary tube A will start moving down. External pressure is now applied on the solution by the piston P so that the level in the capillary tube remains stationary. The applied pressure is recorded on the pressure gauge, which is the osmotic pressure of the solution filled inside the jacket J.

Advantages:

① It is a quick and accurate method.
② The concentration of the solution does not change because flow of solvent is not permitted into solution, so the results obtained by this method are reliable.
③ As the osmotic pressure is balanced by external pressure, there is no strain on membrane and the danger of its bursting is eliminated.

The Laws of Osmotic Pressure:

① Boyle-Van't Hoff Law: This law states that, at a constant temperature, the osmotic pressure (π) of a solution varies inversely as the volume (V) containing 1 mole of a solute,

i.e. $\boxed{\pi \propto \frac{1}{V}}$. (at const. T).

The above relationship is similar to Boyle's law for gases and is known as the Boyle-Van't Hoff law for dilute solutions.

② Charle's-Van't Hoff law:

When osmotic pressures of a sucrose solution was obtained at different temperatures and analyzed by Van't Hoff, it was found that, the ratio of $\frac{\pi}{T}$ is constant irrespective of the temperature.

$\therefore \pi \propto T$.

This is analogous to Charle's law and is known as Charles-Van't Hoff law for dilute solutions.

③ Analogue of gas equation:

as have, $\pi \propto \frac{1}{V}$ ⟶ (I).

$\pi \propto T$ ⟶ (II).

∴ (I) and (II) ⇒ $\pi \propto \frac{T}{V}$.

⇒ $\pi V = R'T$ ⟶ (III),

where R' is a constant.

Eqn (III) analogues to the ideal gas equation, $PV = RT$.

Van't Hoff showed by calculations that the values of R' and the gas constant R are almost identical. $R' = 0.08278\ dm^3$.

∴ $\boxed{\pi V = RT}$ (for dilute sol^{n}s). ⟶ (IV).

where V is the volume of the solution in litres in which one mole of a solute is dissolved. If V ~~refers~~ is volume and in which n_2 moles of a solute are dissolved, then

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

Thermodynamic derivation of expression for calculating osmotic pressure:

Before osmosis, $\mu_1^A > \mu_1^B$ ⟶ (I).

i.e. the chemical potential of the solvent in the solvent chamber A is greater than in the chemical potential in the solution chamber B. When osmosis takes place, the pressure on the solution side increases and at equilibrium, the chemical potential of the solvent in the two chambers becomes equal, i.e.

$\mu_1^A = \mu_1^B$, ⟶ (II).

At equilibrium, the pressure on the solvent is P and that on the solution is $P + \pi$.

∴ $\mu_1^A(T, P) = \mu_1^B(T, P + \pi)$ ⟶ (III).

The chemical potential of the solvent in a solution is a function of temp^r, pressure and composition.

∴ $\mu_1 = f(T, P, x_1)$. ⟶ (IV)

$$\Rightarrow d\mu_1 = \left(\frac{\partial \mu_1}{\partial T}\right)_{P,x_1} dT + \left(\frac{\partial \mu_1}{\partial P}\right)_{T,x_1} dP + \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} dx_1 \longrightarrow (V)$$

At constant T, $dT = 0$,

$$\therefore \left(\frac{\partial \mu_1}{\partial T}\right)_{P,x_1} dT = 0.$$

Also, chemical potential of a component say 1, in an ideal soln is given as, $\mu_1 = \mu_1^\circ + RT \ln x_1 \longrightarrow (VI)$.

$$\therefore \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = RT\, d\ln x$$

$$\Rightarrow \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = \frac{RT}{x_1} \longrightarrow (VII).$$

Again, $\left(\frac{\partial \mu_1}{\partial P}\right)_{T,x_1} = \bar{V} = V_1^\circ$ for an ~~infinity~~ infinitely dilute binary solution $\longrightarrow (VIII)$.

where V_1° is the molar volume of the solvent.

Substituting the various quantities as given by equations (VII) and (VIII) in eqn (V), we get, at constant temperature,

$$d\mu_1 = V_1^\circ dP + RT\, d\ln x_1. \longrightarrow (IX).$$

Integrating eqn (IX) between the limits $P = P$, $x_1 = 1$ and $P = P+\pi$, $x_1 = x_1$, we get,

$$\int_P^{P+\pi} d\mu_1 = V_1^\circ \int_P^{P+\pi} dP + RT \int_{x_1=1}^{x_1=x_1} d\ln x_1 \longrightarrow (X).$$

$$\Rightarrow \mu_1(T, P+\pi) - \mu_1(T,P) = V_1^\circ(P+\pi-P) + RT \ln x_1 \longrightarrow (XI).$$

At equilibrium, the chemical potential of the solvent on the solvent side is equal to the chemical potential of the solvent on the solution side, so that,

$$\mu_1(T, P+\pi) = \mu_1(T,P) \longrightarrow (XII)$$

$$\therefore \text{eqn (XI)} \Rightarrow RT \ln x_1 = -V_1^\circ \pi \longrightarrow (XIII).$$

For a dilute solution, $x_2 << 1$, so that,

$$\ln x_1 = \ln(1-x_2) = -x_2 \longrightarrow (XIV).$$

And we know, $x_2 = \frac{n_2}{n_1+n_2} = \frac{n_2}{n_1}$ for a dilute solution $\longrightarrow (XV)$.

$\therefore$ Eqn (XIII) $\Rightarrow \pi V_1^\circ = x_2 RT = \left(\frac{n_2}{n_1}\right) RT \longrightarrow$ (XVI)

$$\Rightarrow n_1 \pi V_1^\circ = n_2 RT \longrightarrow \text{(XVII)}$$

Now, in a dilute solution, the total volume V is given by,

$$V = n_1 V_1^\circ + n_2 V_2^\circ \approx n_1 V_1^\circ \longrightarrow \text{(XVIII)}.$$

Assuming that in the dilute solution, the addition of solute does not cause much change in the volume of the solvent, we can write,

$$\pi V = n_2 RT$$

<u>Van't Hoff Theory of dilute solutions:</u>

The law states that, "The osmotic pressure of a dilute solution is equal to the ~~preserve~~ pressure which the dissolved substance would exert if it is existed as a gas at the same temperature and occupied the same volume as the solution".

We know,

$$\pi V = n_2 RT.$$

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

$$\boxed{\Rightarrow \pi = C_2 RT} \longrightarrow (1).$$

Eqn (1) is known as the Van't Hoff equation for osmotic pressure of a dilute solution where, C_2 is the molar concentration of the solute in the solution.

<u>Determination of Molar Mass from osmotic pressure measurement:</u>

We know, Van't Hoff equation,

$$\pi = C_2 RT.$$

$$\Rightarrow \pi = \left(\frac{\omega_2}{M_{\omega_2} V}\right) RT. \longrightarrow (1).$$

where ω_2 is the weight of the solute in grams dissolved in V litres of the solution and M_{ω_2} is its molecular weight.

$$(1) \Rightarrow \boxed{M_{\omega_2} = \frac{\omega_2 RT}{\pi V}} \longrightarrow (11).$$

Eqn (11) can be used to determine the molar mass of a

non-volatile solute from the measurement of the osmotic pressure of its dilute solution in a given solvent.

Relation between vapour pressure lowering and osmotic pressure:

Let us suppose an aqueous solution is contained in an inverted thistle funnel which is closed by a semipermeable membrane at the bottom and is immersed in pure water contained in a beaker. Let the entire apparatus be enclosed in a bell jar which is evacuated as shown in the figure.

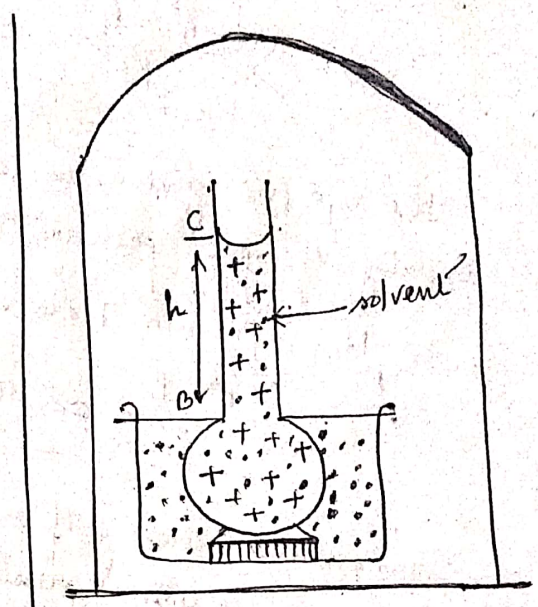


Fig: Vapour pressure lowering and osmotic pressure.

Due to osmosis, water rises to a height h (say) in the thistle funnel.

Thus, $\pi = h\rho_s \longrightarrow (I)$

where, ρ_s is the density of the solution & π is the osmotic pressure.

Let P_1° be the vapour pressure of water at B. The pressure of water vapour at C will be less than P_1°. The difference in the pressure of water vapour at B and C must be equal to the pressure of column of water vapour of height, h.

i.e $P_1^\circ - P_1 = h\rho_v \longrightarrow (II)$

where ρ_v is the density of water vapour.

P_1 is the ~~den~~ pressure of water vapour at C.

Putting the value of h in eqn (II),

$$P_1^\circ - P_1 = \frac{\pi}{\rho_s}\rho_v \longrightarrow (III)$$

Let $M\omega_1$ be the molar mass of vapour and V_1 its molar volume, then,

$$\rho_v = \frac{M\omega_1}{V_1} \longrightarrow (IV)$$

∵ For 1 mole of vapour,

$$P_1 V_1 = RT \longrightarrow (v)$$ (assuming the ~~vapor~~ vapour behaves as an ideal gas)

$$\therefore \rho_v = \frac{M_{\omega_1} P_1^\circ}{RT} \longrightarrow (vi).$$

∴ Putting the value of ρ_v in eqn (iii)

$$P_1^\circ - P_1 = \frac{\pi}{\rho_s} \times \frac{M_{\omega_1} P_1^\circ}{RT}.$$

$$\Rightarrow \boxed{\frac{P_1^\circ - P_1}{P_1^\circ} = \frac{\pi M_{\omega_1}}{\rho_s RT}} \longrightarrow (vii)$$

The eqn (vii) gives the relation between the relative lowering of vapour pressure and the osmotic pressure.

∵ M_{ω_1}, ρ_s and T are constant for a given solvent.

$$\therefore \boxed{\frac{P_1^\circ - P_1}{P_1^\circ} \propto \pi}$$

Thus relative lowering of vapour pressure is directly proportional to osmotic pressure.

Relation between osmotic pressure and vapour pressure lowering of an ideal solution (Thermodynamic aspect).

Let, chemical potential of a pure solvent be μ° and that of the solution be μ. Let π be the osmotic pressure applied on the solution to bring about equilibrium between the solvent and the solution.

Thus, the total external pressure on the soln side is $(1+\pi)$ atm while the external press^r on the pure solvent side remains 1 atm.

∵ Since, the system is in osmotic ~~pressure~~ equilibrium

$$\therefore \mu^\circ = \mu + \Delta\mu$$

$$\Rightarrow \mu - \mu^\circ = -\Delta\mu \longrightarrow (1).$$

We know, $\mu = \mu^0 + RT \ln a \longrightarrow$ (II)

where a is the activity of the solvent in the solution.

eqn (I) and (II) $\Rightarrow$ $-\Delta\mu = RT \ln a \longrightarrow$ (III).

If the soln is ideal, $a = p/p^0$

$\therefore$ (III) $\Rightarrow$ $-\Delta\mu = RT \ln\left(\frac{p}{p^0}\right) \longrightarrow$ (IV).

where p^0 is the vapour pressure of the pure solvent while p is the vapour pressure of the solvent in the solution at the same temperature.

Again, $dG = Vdp$ at const. ~~temp~~ T $\longrightarrow$ (V).

For partial molar quantities,

$$\overline{dG} = \bar{V}dp \longrightarrow \text{(VI)}.$$

$\therefore$ $\bar{G} = \mu$.

$$\therefore \quad d\mu = \bar{V}dp \longrightarrow \text{(VII)}.$$

where $\bar{V}$ is the partial molar volume of the solvent in the solution.

Integrating eqn (VII), between limits μ of the solution at 1 atm pressure and μ' of the solvent at $(1+\pi)$ atm press,

$$\int_{\mu}^{\mu'} d\mu = \int_{1}^{1+\pi} \bar{V}dp \longrightarrow \text{(VIII)}.$$

Let, $\bar{V}$ be independent of pressure.

$$\therefore \mu' - \mu = \Delta\mu = \bar{V}(1+\pi-1) = \bar{V}\pi \longrightarrow \text{(IX)}.$$

Putting the value of $\Delta\mu$ in eqn. (IV),

$$\boxed{\pi = \frac{RT}{\bar{V}} \ln\left(\frac{p^0}{p}\right)} \longrightarrow \text{(X)}.$$

Equation (X) represents the desired relation between osmotic pressure and lowering of vapour pressure.

* If the solution is infinitely dilute, $\bar{V}$ may be taken as V^0.

$$\therefore \boxed{\pi = \frac{RT}{V^0} \ln\left(\frac{p^0}{p}\right)}$$

Reverse Osmosis:

Let us consider a solution separated from the pure solvent by a semipermeable membrane. If the pressure applied on the solution is more than the osmotic pressure, then the solvent will start flowing from the solution towards the pure solvent. This phenomenon is known as reverse osmosis.

This technique is now being often extensively employed for getting drinking water from the sea water, particularly in Gulf countries.

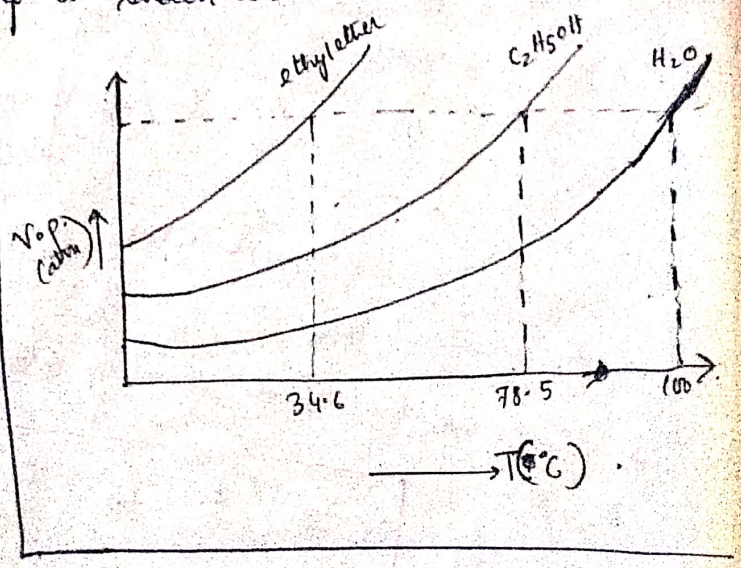
Elevation of boiling point:

~~Rising temperature causes raising vp of a liquid~~. ~~This is quite~~

The boiling point, T_b, of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure. When a non-volatile solute is added to a liquid, the vapour pressure of the liquid is decreased. Hence, it must be heated to a higher temperature in order that its vapour pressure becomes equal to the atmospheric pressure. This means that the boiling point of a solution will always be higher than the boiling point of pure solvent. This is known as elevation of boiling point.

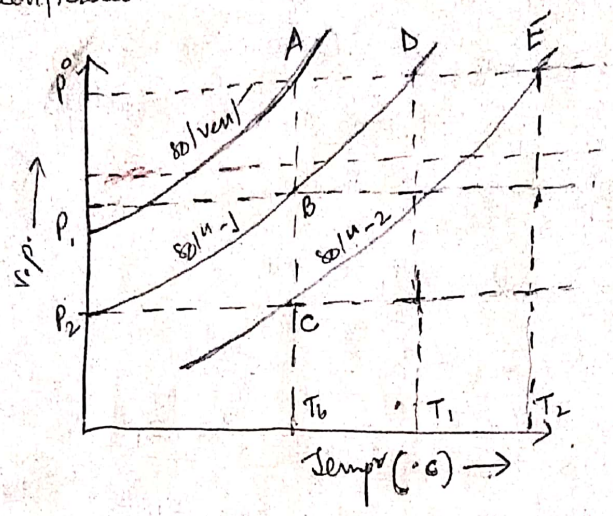
For some common liquid, the variation of vapour pressure with temp^r is shown below —

Liquid with weak intermolecular force have relatively high vapour pressure. The temp^r at which the vapour press^r of a liquid is equal to the boiling point of a liquid, the boiling point of a liquid changes with change in external pressure.



Hence, the temp^r at which a liquid shows pressure of 1 atm is called normal boiling point.

The lowering of vapour pressure according to Raoult's Law depends on the amount of solute dissolved. The following figure shows the change in vapour pressure with temperature for pure solvent and solution at different concentration.



It is quite clear that dissolution of a non-volatile substance in a volatile ~~solute~~ solvent causes rise in boiling point. The rise in boiling point however depends on the amount of solute dissolved in the solution. The ~~causes are~~ curves are almost parallel as the molar heat of vapourization for the sol^n is nearly equal to that of the pure solvent. Thus ~~ABD and~~ ΔABD and ΔACE can be considered as two similar triangles.

Then $\frac{AE}{AD} = \frac{AC}{AB}$ ⟶ (i)

From the graph,

$$\frac{T_2 - T_b}{T_1 - T_b} = \frac{P^0 - P_2}{P^0 - P_1} \longrightarrow \text{(ii)}$$

$$\Rightarrow \frac{(\Delta T)_2}{(\Delta T)_1} = \frac{(\Delta P)_2}{(\Delta P)_1} \longrightarrow \text{(iii)}$$

Hence, $\Delta T_b \propto \Delta P \longrightarrow$ (iv)

From Raoult's Law,

$$\Delta P = P^0\left(\frac{n_2}{n_1+n_2}\right) \longrightarrow (V)$$

where n_1 is mole of solⁿ

n_2 is mole of solute.

$$\therefore \quad \Delta P = P^0\left(\frac{n_2}{n_1}\right) = P^0\left(\frac{n_2}{w_1/M_1}\right)$$

$$\Rightarrow \quad \Delta P = P^0\left(\frac{M_1 n_2}{w_1}\right).$$

For a solvent and at any temp^r,

P^0 and M_1 are constant.

Hence, $\Delta P = \frac{n_2}{w_1}$

But, $\Delta T_b \propto \Delta P$.

$$\therefore \Delta T_b \propto \frac{n_2}{w_1}$$

$$\Rightarrow \boxed{\Delta T_b = K_b \frac{n_2}{w_1}}$$

when, $n_2 = 1$ mole and $w_1 = 1g$. then

$$\Delta T_b = K_b.$$

where K_b is called boiling point constant or ebullioscopic constant. This may be considered as the elevation of boiling point of when one mole of the ~~solute~~ solvent. However, in practice, the boiling point const. called molal elevation constant or molal boiling point constant is taken as the elevation of boiling point produced when 1 mole of the solute is dissolved in 100 g of the solvent.

$$\therefore \Delta T_b = K_b \frac{n_1}{w_1} \times 1000.$$

$$\Rightarrow \boxed{\Delta T_b = K_b\left(\frac{w_2 \times 1000}{w_1 M_2}\right)}$$

$$\Rightarrow \boxed{\Delta T_b = \frac{R T_b^2 \quad w_2}{\Delta H_{vap} \quad w_1 M_2}} \qquad \left[\because K_b = \frac{R T_b^2}{\Delta H_{vap} \times 1000}\right]$$

Thermodynamic derivation of elevation of boiling point:

Applying the Clausius eqⁿ for vapour pressure, temperature curve for the solⁿ 1 and solvent we have, at point D,

$$\ln P^{\circ} = \frac{-\Delta H_v}{RT_1} + \text{const.} \longrightarrow (I)$$

At point B,

$$\ln P_1 = -\frac{\Delta H_v}{RT_b} + \text{const} \longrightarrow (II)$$

At equilibrium, values of const are equal.

$$\therefore \ln\left(\frac{P_1}{P_0}\right) = -\frac{\Delta H_v}{R}\left(\frac{1}{T_b} - \frac{1}{T_1}\right)$$

$$= -\frac{\Delta H_v}{R}\left(\frac{T_1 - T_b}{T_1 T_b}\right) \longrightarrow (III)$$

As T_1 and T_b are not much different.

$$\therefore T_1 T_b \approx T_b^{\circ}.$$

Remembering that, $T_1 - T_b = \Delta T_b$ and

$$\frac{P_1}{P_0} = x_1 = \text{mole fraction of the solvent}$$

$= 1 - x_2$ where, x is mole fraction of the solute.

$$\therefore \ln(1 - x_2) = \frac{-\Delta H_v}{R}\left(\frac{\Delta T_b}{\Delta T_b^{\circ}}\right)$$

For dilute solⁿ,

$$\ln(1 - x_2) \approx -x_2.$$

$$\Rightarrow -x_2 = -\frac{\Delta H_v}{R}\left(\frac{\Delta T_b}{T_b^{\circ}}\right).$$

$$\Rightarrow x_2 \frac{R}{\Delta H_v} T_b^{\circ} = \Delta T_b.$$

$$\Rightarrow \Delta T_b = \frac{T_b^{\circ} R}{\Delta H_v} x_2 \longrightarrow (IV)$$

If n_1 and n_2 are the no. of moles of the solvent and the solute respectively then,

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

If w_1 g of the solved molecule of molecular weight M_1 dissolves in w_2 gm of solute of molecular weight M_2 then,

$$x_2 = \frac{w_2/M_2}{w_1/M_1}$$

$$= \frac{w_2 \cdot M_1}{w_1 \cdot M_2} \longrightarrow (v)$$

$\because \Delta H_v = M_1 l_e$

where, l_e = latent heat of vapourization of solvent.

or $\Delta T_b = K_b m$.

$$\Rightarrow K_b = \frac{RT_b}{1000} l_e = \text{const.}$$

$$\therefore \Delta T_b = \frac{RT_b^2}{l_e M_1} \times \frac{w_2 M_1 \times 1000}{w_1 \times M_2}$$

$$= \frac{RT_b^2}{l_e} \times \frac{1000\, w_2}{M_2 w_1}$$

where, m is the molality of solution which is the no. of moles of solute dissolve in 1000 gm of the solvent. Here, $\frac{w_2}{M_2}$ moles of solute is dissolves in w_1 g of solvent.

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

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

<u>Determination of molecular weight of the solute:</u>

The molecular weight of a substance can be determine from the measurement of elevation of boiling point for the solution of that substance.

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

$$\boxed{\Rightarrow M_2 = \frac{K_b\, 1000\, w_2}{\Delta T_b \times w_1}}$$

All the quantities of R.H.S. are measurable and the method is used to determine the molecular weight of only non-volatile or non-electrolytic solute.

Determination of Boiling point elevation:

(a) The Landsberger's Method:

In this method, the vapour of the boiling solvent is used to heat the solution. The apparatus consists of a flask A which contains the pure solvent and is connected through a delivery tube to a graduated tube B which also contains a small quantity of the solvent. A small hole H, towards the top of the graduated tube, permits its communication with the outer vessel V. A condenser C, helps to condense the escaping vapour. A thermometer is placed in the tube B ~~and~~ within the liquid. A stream of the solvent from the flask A enters the graduated tube B and condenses there. The latent heat of condensation raises the temperature of the solvent to the boiling point. The temp is noted when constant and it gives the boiling point of the pure solvent.

A weight amount of the solute under examination is then added into the tube B and the process is repeated till the temperature is again constant. This gives the boiling point of the solution and the volume of the solution is noted. Knowing the density of the solvent, the mass of the solvent present in the solution can be calculated.

The difference between the two boiling points gives the boiling point elevation.

Fig: Landsberger's boiling point apparatus.

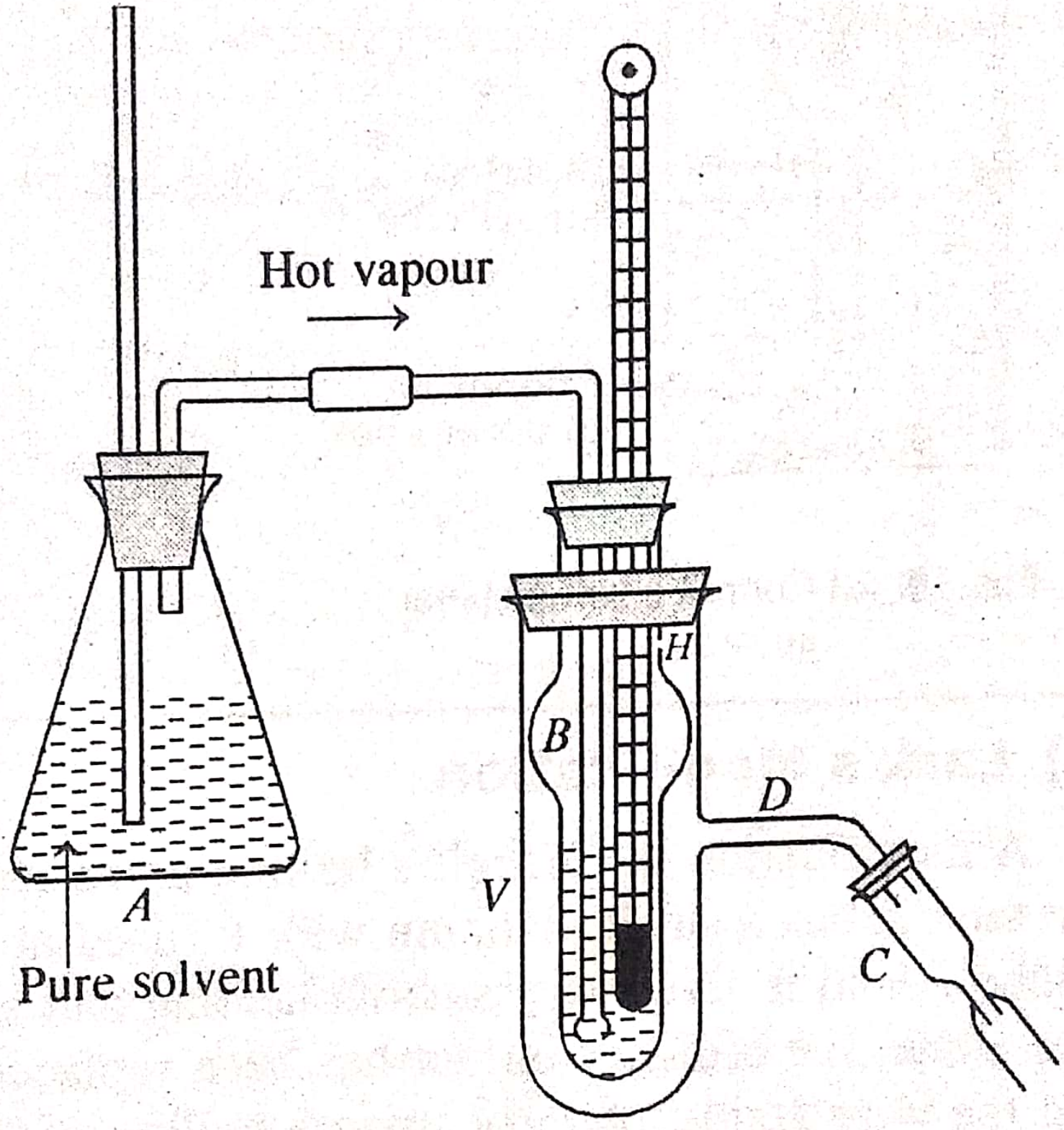


Fig. 9. Landsberger's boiling point apparatus.

Imp.

(b) Cottrell's Method :

The apparatus consists of a boiling tube A which is graduated and contains the liquid under ~~the~~ examination. An inverted funnel tube placed in the boiling tube collects the bubbles rising from a few fragments of a porous pot in the liquid. When the liquid starts boiling, it pumps a stream of liquid and vapour over the bulb of the Beckmann thermometer held a little above the liquid. In this way the bulb is covered with a thin layer of boiling liquid.

The vapours of the solvent rising above ~~the~~ are condensed in the condenser and are returned back. After determining the boiling point of the pure solvent the contents in the boiling tube A are cooled and a weighed amount of the solute is added and another reading of the boiling point of the solution on the Beckmann thermometer taken. The volume of the solution is noted and from the density of the solvent, the mass of the solvent present in the solution can be calculated. ~~as in~~ ~~by calculating~~ The difference between two boiling points gives the boiling point elevation.

fig: Cottrell's boiling point apparatus

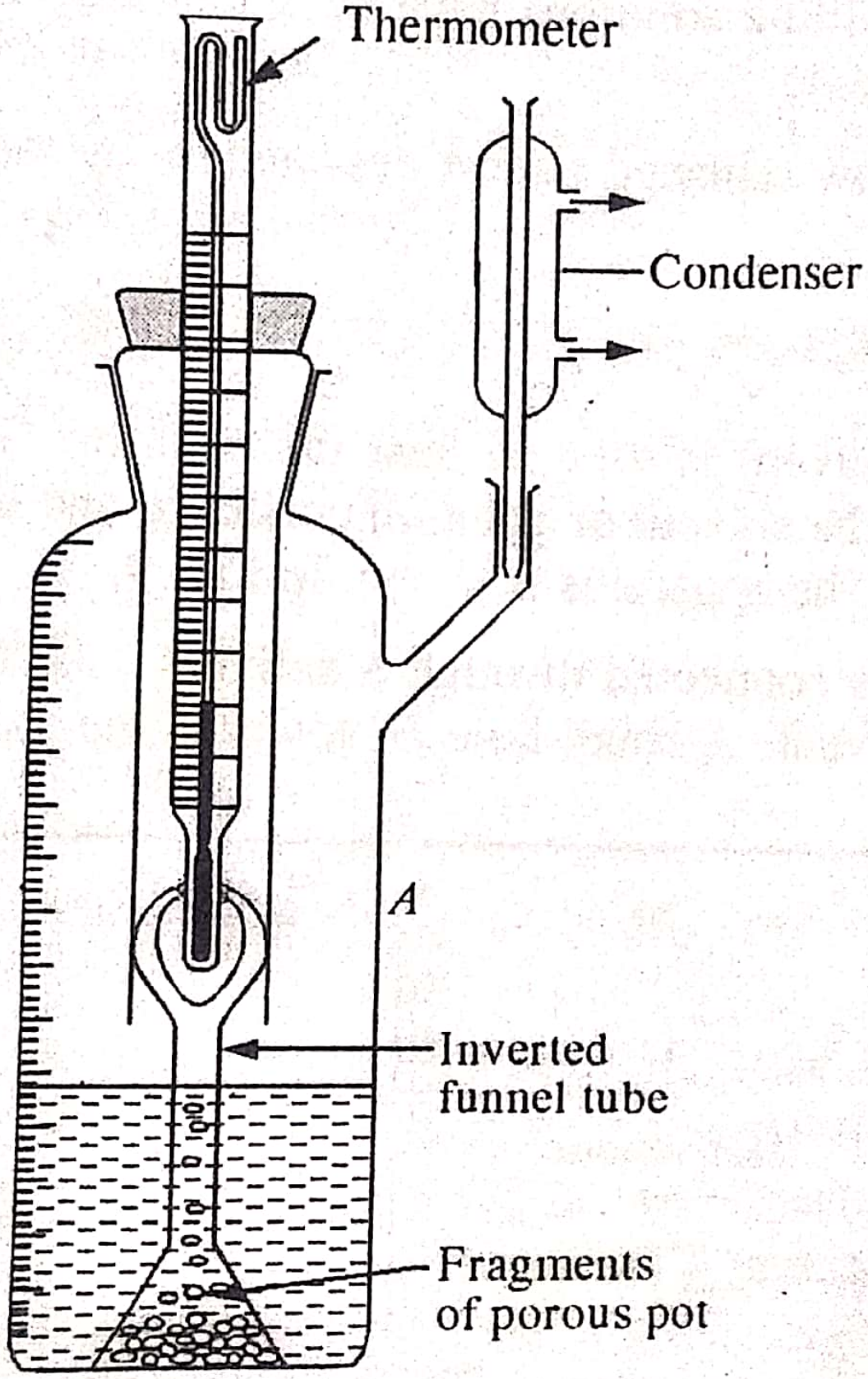


Fig. 10. (*a*) Cottrell's boiling point apparatus.

Depression of freezing point:

Freezing point is the temperature at which solid and liquid states of a substance are in equilibrium and have the same vapour pressure.

Let T_0 be the freezing point of the solvent & T be the freezing point of the solution.

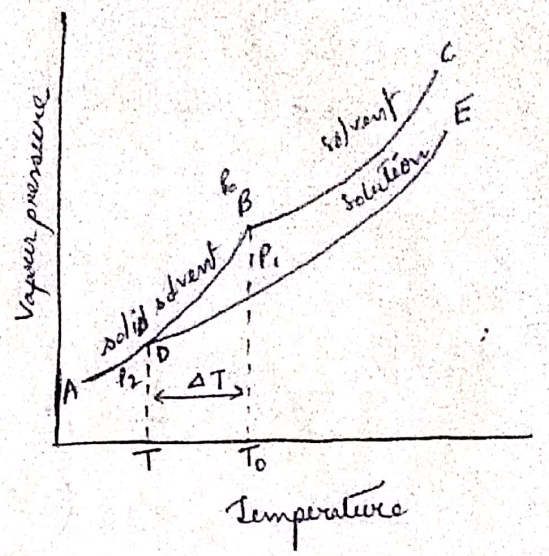


Fig: Freezing point depression.

Hence, ΔT_f i.e. depression in freezing point is given by $T_0 - T$. Let, P_1 is the vapour pressure of the solution at temp^r T_0 and P_2 is the vapour press^r of the sol^n at temp^r T. considering the curve DE,

$\therefore$ Applying Clausius - Clapeyron eq^n,

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_v}{R} \times \frac{\Delta T_f}{T_0 T} \longrightarrow (I)$$

where ΔH_v is the molar heat of vaporisation of the pure solvent at its normal freezing point T_0.

Again, considering the curve AB of the solid solvent, P_0 is the vapour pressure of the solid solvent at temp^r T_0 and P_2 is the vapour pressure of the solid solvent at temp^r T,

$\therefore$ Applying Clausius - Clapeyron eq^n,

$$\ln \frac{P_0}{P_2} = \frac{\Delta H_s}{R} \times \frac{\Delta T_f}{T_0 T} \longrightarrow (II)$$

where ΔH_s is the molar heat of sublimation of the solid solvent.

eq^n (II) - (I) $\Rightarrow$ $$\ln \frac{P_0}{P_2} - \ln \frac{P_1}{P_2} = \frac{\Delta H_s - \Delta H_v}{R} \left[\frac{\Delta T_f}{T_0 T}\right] \longrightarrow (III)$$

$$\Rightarrow \ln \frac{P_0}{P_1} = \frac{\Delta H_f}{R} \left[\frac{\Delta T_f}{T_0 T}\right] \longrightarrow (IV)$$

where,

$\Delta H_f = (\Delta H_s - \Delta H_v)$ is the molar heat of fusion of the ~~solvent~~ solvent.

When the solution is dilute,

$T = T_0$,

$$\therefore \ln \frac{P_0}{P_1} = \frac{\Delta H_f}{R} \times \frac{\Delta T_f}{T_0^2} \longrightarrow (v)$$

Now,

$$\ln \frac{P_0}{P_1} = \cancel{\ln \frac{P_0}{P_1}} - \ln \frac{P_1}{P_0}$$

$$= -\ln \left(\frac{P_0 - P_0 + P_1}{P_0} \right)$$

$$= -\ln \left(1 - \frac{P_0 - P_1}{P_0} \right)$$

$$\Rightarrow \ln \frac{P_0}{P_1} = \frac{P_0 - P_1}{P_0} \longrightarrow (vi)$$

$\because \frac{P_0 - P_1}{P_0}$ is quite small and

$\ln(1-x) = -x$ when x is small.

From eqn (v) and (vi),

$$\frac{\Delta H_f}{R} \left[\frac{\Delta T_f}{T_0^2} \right] = \frac{P_0 - P_1}{P_0} \longrightarrow (vii)$$

By Raoult's Law, for very dilute solutions,

Relative lowering of vapour $= x_2$ mole fraction of solute

i.e. $\frac{P_0 - P_1}{P_0} = x_2 = \frac{n_2}{n_1 + n_2}$.

But for a dilute solution, n_2 is negligible as compared to n_1.

$$\frac{P_0 - P_1}{P_0} = \frac{n_2}{n_1} \longrightarrow (viii)$$

Eqn (vii) and (viii)

$$\Rightarrow \frac{\Delta H_f}{R} \left[\frac{\Delta T_f}{T_0^2} \right] = \frac{n_2}{n_1}$$

$$\Rightarrow \boxed{\Delta T_f = \frac{n_2}{n_1} \times \frac{R T_0^2}{\Delta H_f}} \longrightarrow (ix)$$

If w_2 g of a solute of molar mass M_2 is dissolved in w_1 g of a solvent of molar mass M_1. then,

$$\Delta T_f = \frac{RT_0^2}{\Delta H_f} \times \frac{w_2}{M_2} \times \frac{M_1}{w_1} \longrightarrow (X)$$

Now, $\frac{w_2}{M_2}$ = no. of moles of solute.

If $w_1 = 1kg$, then, $\frac{w_2}{M_2} = m$ (molality).

$$\therefore \text{Eqn } (X) \Rightarrow \boxed{\Delta T_f = \frac{RT_0^2 M_1}{\Delta H_f} \times m} \longrightarrow (XI)$$

$$\Rightarrow \Delta T_f = K_f m$$

where $K_f = \frac{RT_0^2 M_1}{\Delta H_f}$ is called molal freezing point depression constant or cryoscopic constant of the solvent.

$$\therefore K_f = \frac{\Delta T_f}{m}$$

If $m = 1$ mol/kg

$K_f = \Delta T_f$.

Thus cryoscopic constant may be defined as the depression in the freezing point of the given solvent when one mole of the non-volatile solute is dissolved in 1 kg of the solvent.

Thermodynamic derivation of depression in freezing point:

Let, $(\mu_1^\circ)^l$ is the chemical potential of the pure liquid 1 and x_1^l is its mole fraction in the solution. ~~and~~ μ_1^s be the chemical potential of ~~the~~ the solid solvent 1 and μ_1^l be the chemical potential of the liquid 1.

$\therefore$ At eqm, $\mu_1^s = \mu_1^l = (\mu_1^\circ)^l + RT \ln x_1^l \longrightarrow (1)$,

For a small change in T and composition at equilibrium,

$$d\mu_1^s = d\mu_1^l \longrightarrow (II)$$

$\because \mu_1^s = f(T, P)$ and $\mu_1^l = f(T, P, x_1)$

$$\therefore d\mu_1^s = \left(\frac{\partial \mu_1^s}{\partial T}\right)_P dT + \left(\frac{\partial \mu_1^s}{\partial P}\right)_T dP \longrightarrow (III)$$

At constant, P, $dP = 0$, so that,

$$d\mu_1^s = \left(\frac{\partial \mu_1^s}{\partial T}\right) dT = -S_1^s dP \longrightarrow (IV)$$

Similarly,

$$d\mu_1^l = \left(\frac{\partial \mu_1^l}{\partial T}\right)_{P, x_1} dT + \left(\frac{\partial \mu_1^l}{\partial P}\right)_{T, x_1} dP + \left(\frac{\partial \mu_1^l}{\partial x_1}\right)_{T,P} dx_1 \longrightarrow (V)$$

$$\Rightarrow d\mu_1^l = -\bar{S}_1^l dT + \left(\frac{\partial \mu_1^l}{\partial x_1}\right)_{T,P} dx_1 \text{ at constant } P \longrightarrow (VI)$$

For an infinitely dilute binary solution,

$$\bar{S}_1 = S$$

$\therefore$ Eq^n (VI)

$$\Rightarrow d\mu_1^l = -S_1^l dT + \left(\frac{\partial \mu_1^l}{\partial x_1}\right)_{T,P} dx_1 \text{ at const } P$$

For an ideal solution,

$$d\mu_1^l = -S_1^l dT + RT d\ln x_1^l \longrightarrow (VII)$$

At eq^m, $\mu_1^l = \mu_1^s$ ~~so that~~

$$\Rightarrow d\mu_1^l = d\mu_1^s$$

$\therefore$ from eq^{n}s, (IV) and (VII),

$$-S_1^s dT = -S_1^l dT + RT d\ln x_1^l$$

$$\Rightarrow (S_1^l - S_1^s) dT = RT d\ln x_1^l$$

$$\Rightarrow \Delta S_{fus} \cdot dT = RT d\ln x_1^l \longrightarrow (VIII)$$

where, ΔS_{fus} is the molar entropy of fusion.

$$\therefore \Delta S_f = \frac{\Delta H_f}{T}$$

$$\therefore \text{Eq}^n \text{ (VIII)} \Rightarrow d\ln x_1^l = \left(\frac{\Delta H_f}{RT}\right) \cdot dT \longrightarrow (IX)$$

where, ΔH_f is the molar enthalpy of fusion.

Assuming that molar enthalpy of fusion remains constant over the temperature range,

$$\text{Eq}^n \text{ (IX)} \Rightarrow \int_1^{x_1} d\ln x_1' = \frac{\Delta H_f}{R}\int_{T_0}^{T_f} \frac{dT}{T^2} \quad \left\{ \begin{array}{l} At, x_1 = 0, T = T_0. \\ At, x_1 = x, T = T_f. \end{array} \right.$$

$$\Rightarrow \ln x_1' = -\frac{\Delta H_f}{R}\left[\frac{1}{T_{fus}} - \frac{1}{T_0}\right],$$

$$\Rightarrow \ln x_1' = -\frac{\Delta H_f}{R}\left[\frac{\Delta T_f}{T_0 T_{fus}}\right] \longrightarrow \text{(X)}$$

where, $\Delta T_f = (T_0 - T_f)$ is the depression in freezing point of the solution.

For a dilute solution, $T_0 = T_f$ and $\ln x_1 = \ln(1-x_2) = -x_2$.

$$\therefore \text{Eq}^n \text{ (X)} \Rightarrow x_2 = \frac{\Delta H_f}{R}\left[\frac{\Delta T_f}{T_0^2}\right] \longrightarrow \text{(XI)}.$$

where, $x_2 = \frac{n_2}{n_1+n_2} = \frac{n_2}{n_1} = \frac{w_2 \times M_1}{M_2 \times w_1}$ for a dilute sol^n.

$$\therefore \text{Eq}^n \text{ (XI)} \Rightarrow \frac{\Delta H_f}{R}\left[\frac{\Delta T_f}{T_0^2}\right] = \frac{w_2 \times M_1}{M_2 \times w_1} \longrightarrow \text{(XII)}.$$

If $w_1 = 1\,kg$, Then $\frac{w_2}{M_2} = m$ (molality) of the sol^n.

$$\therefore \text{Eq}^n \text{ (XII)} \Rightarrow \frac{\Delta H_f}{R} \times \frac{\Delta T_f}{T_0^2} = m M_1.$$

$$\Rightarrow \boxed{\Delta T_f = \frac{R T_0^2 M_1}{\Delta H_f} \cdot m}.$$

$$\Rightarrow \Delta T_f = K_f \cdot m,$$

where, $K_f = \frac{R T_0^2 M_1}{\Delta H_f}$ is ~~called~~ a constant called molal freezing point depression constant or cryoscopic const. of the solvent.

Determination of molar mass from freezing point depression:

We have,

$$\frac{\Delta H_f}{R} \times \frac{\Delta T_f}{T_0^2} = \frac{\omega_2 \times M_1}{M_2 \times \omega_1}$$

$$\Rightarrow M_2 = \frac{R T_0^2 M_1}{\Delta H_f \, \Delta T_f} \times \frac{\omega_2}{\omega_1}$$

$$\Rightarrow M_2 = \frac{K_f}{\Delta T_f} \cdot \frac{\omega_2}{\omega_1} \, kg\,mol^{-1} \left[\because K_f = \frac{R T_0^2 M_1}{\Delta H_f} \right]$$

$$\boxed{\Rightarrow M_2 = \frac{K_f}{\Delta T_f} \cdot \frac{\omega_2}{\omega_1} \times 1000 \, g\,mol^{-1}}$$

Thus, knowing the value of ~~ΔT_f~~ ΔH_f or K_f of the solvent and by measuring ΔT_f of a solution of known concentration, M_2 can be calculated.

Determination of freezing point depression :

(a) The Beckmann Method: The apparatus consists of a freezing tube A with a side arm B through which a known amount of a solute is introduced. A stopper carrying a Beckmann thermometer and a stirrer is fitted into the freezing tube. A guard tube C surrounds the freezing tube to prevent rapid cooling of the contents of freezing tube. The whole assembly is placed in a wide vessel V which contains a freezing mixture giving a temp about 5°C below the freezing point of the pure solvent.

A known amount of the pure solvent is placed in the tube A and cooled with gentle continuous stirring. The temp will gradually fall by about 0.5 – 2° below the freezing point. Vigorous stirring is then set in when solid starts separating and the temperature rises rapidly. This temp is noted which is the freezing point of the solvent.

Then the tube A is taken out, warmed to melt the solid and a known amount of the solute is added through the side tube B. When the solute passes into the solution, the tube A is put back in its original position and the freezing point is determined in the same manner as before. The difference between the two readings gives the freezing point depression.

Fig: Beckmann's freezing point apparatus.

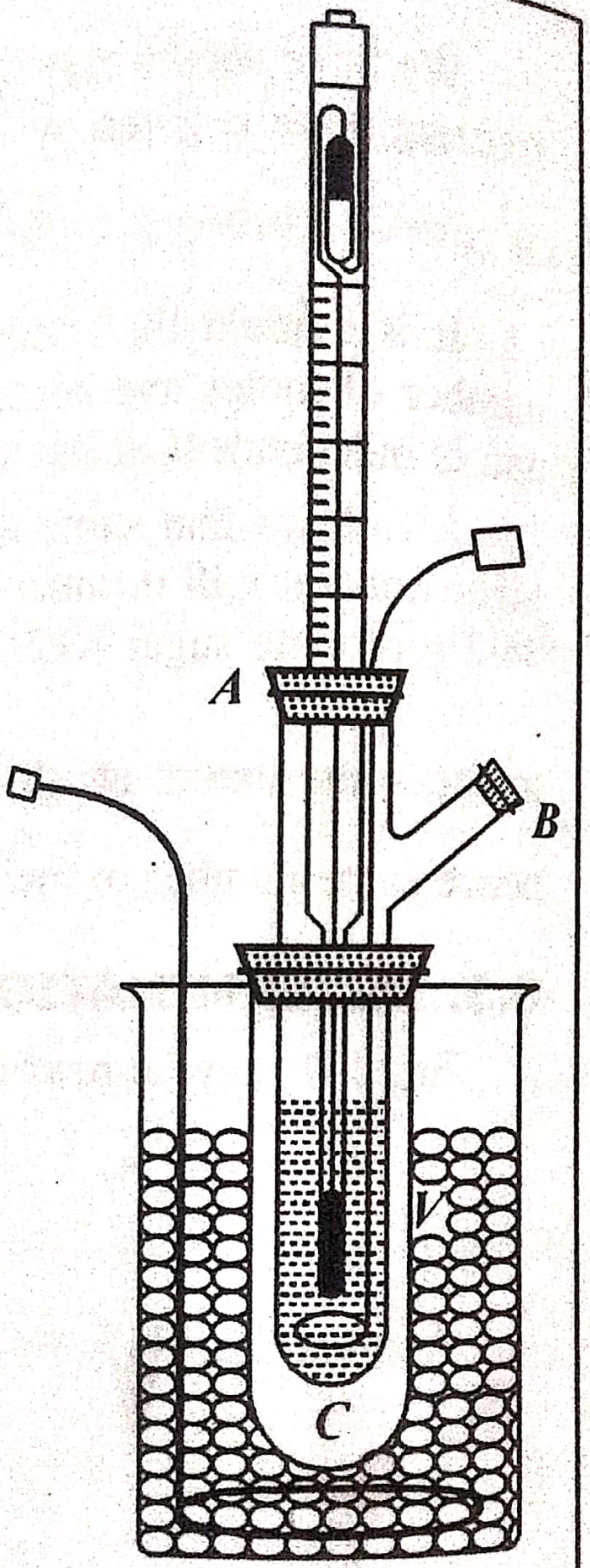


Fig. 12. Beckmann's freezing point apparatus.

(E) The Rast Method:

Rast devised this method for determining molar masses of solutes which are soluble in camphor. Camphor has an extraordinary high value of molal depression constant which is 37.7 K kg mol^{-1} i.e. when one of mole of a solute is dissolved in 1 kg of camphor, the depression caused in its freezing point is 37.7°C whereas the same amount when dissolved in 1 kg of water lowers the freezing point by 1.86°C only. Thus, the freezing point depression can be measured by ordinary thermometer.

A small amount of powdered camphor is first introduced into a thin-walled capillary tube and its melting point is determined. This is taken as the freezing point of the pure solvent. A known amount of the solute is then added to a known amount of camphor and the two are fused together to get an intimate mixture. The melt is cooled to get a solid which is powdered and a small amount of it is taken in a capillary tube for determining melting point as before. This is taken as the freezing point of the solution. The difference in the two freezing points gives the freezing point depression.

The Van't Hoff factor and Abnormal Results:

(1) Association: Association takes place when two or more molecules of the solute in non-aqueous solution associate to form bigger molecule. Thus, the no. of effective molecules or particles decreases and consequently the osmotic pressure, the elevation of boiling point or the depression of freezing point ~~also~~ becomes less than the calculated value on the basis of single molecule.

e.g. Acetic acid in benzene and chloroacetic acid in naphthalene.

The molar mass of ~~benzene~~ acetic acid in benzene is 118 instead of 60. i.e. It forms dimer $(CH_3COOH)_2$ when dissolved in benzene.

(2) <u>Dissociation</u>: Dissociation takes place when electrolytes (acids, bases and salts) in aqueous solutions break down into positively and negatively charged ions.

e.g. NaCl in aqueous solution exists as Na^+ and Cl^- ions. Hence, the values of measured colligative property is much higher than those calculated on the basis of undissociated molecules.

Hence, in order to account for these abnormal cases, Van't Hoff introduced a factor i, known as the Van't Hoff factor which is defined as,

Imp.

$$i = \frac{\text{Observed osmotic effect}}{\text{Normal osmotic effect}}$$

$$= \frac{\text{observed colligative property}}{\text{normal colligative property}}$$

∵ Colligative properties vary inversely as the molar masses of the solute, hence,

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

<u>Degree of Association</u>:

Let, one mole of a solute is dissolved in a given amount of a solvent.

Let, n simple molecules combine to form an associated molecule i.e. $nA \rightleftharpoons (A)_n$.

Let α be the degree of association, then,

The no. of unassociated moles $= 1-\alpha$

The no. of associated moles $= \frac{\alpha}{n}$

$\therefore$ The no. of effective moles $= 1-\alpha+\alpha/n$

$$\therefore i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

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

Thus, as the value of n is known, i can be easily calculated.

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

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

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

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

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

Degree of dissociation:

Let, one mole of a uni-univalent electrolyte like KCl dis be dissolved in a given amount of water. Let α be its degree of dissociation.

$$\therefore \quad KCl \rightleftharpoons K^+ + Cl^-$$

At eqm $\quad 1-\alpha \qquad \alpha \qquad \alpha$

Thus, the total no. of moles after dissociation

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

Hence, ~~Observed~~ $\frac{M_{normal}}{M_{observed}} = \frac{1+\alpha}{1}$,

$$\Rightarrow \frac{M_n}{M_o} - 1 = \alpha.$$

$$\Rightarrow \boxed{\alpha = \frac{M_n - M_o}{M_o}}.$$

Thus, knowing the observed molar mass, the degree of dissociation α can be easily calculated.