Properties of Dilute Solutions

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Solution

A solution is a homogeneous mixture of two or more substances on molecular level. The constituent of the mixture present in a smaller amount is called the Solute and the one present in a larger amount is called the Solvent.

Concentration of solution = $\dfrac{Quantity\ of\ solute}{Volume\ of\ solution}$

State of Solution	State of Solvent	State of Solute	Example
Gas	Gas	Gas	Air
Liquid	Liquid	Gas	Oxygen in water
Liquid	Liquid	Liquid	Alcohol in water
Liquid	Liquid	Solid	Salt in water
Solid	Solid	Gas	Hydrogen in palladium
Solid	Solid	Liquid	Mercury in silver
Solid	Solid	Solid	Silver in gold

Ways of expressing concentrations

(*a*) Percent by weight = $\dfrac{Weight\ of\ solute}{Weight\ of\ solution} \times 100$

(*b*) Mole fraction = $\dfrac{Moles\ of\ solute}{Moles\ of\ solute + Moles\ of\ solvent}$

(*c*) Molarity = $\dfrac{Moles\ of\ solute}{Volume\ in\ litres}$

(*d*) Molality = $\dfrac{Moles\ of\ solute}{Mass\ of\ solvent\ in\ kg}$
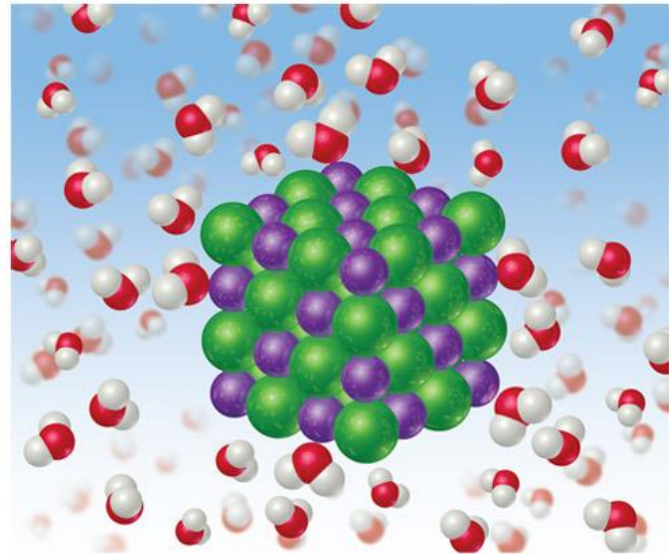
(e) Normality = $\dfrac{Equivalent\ weight\ of\ solute}{Volume\ of\ solution\ in\ litre}$

Solutions

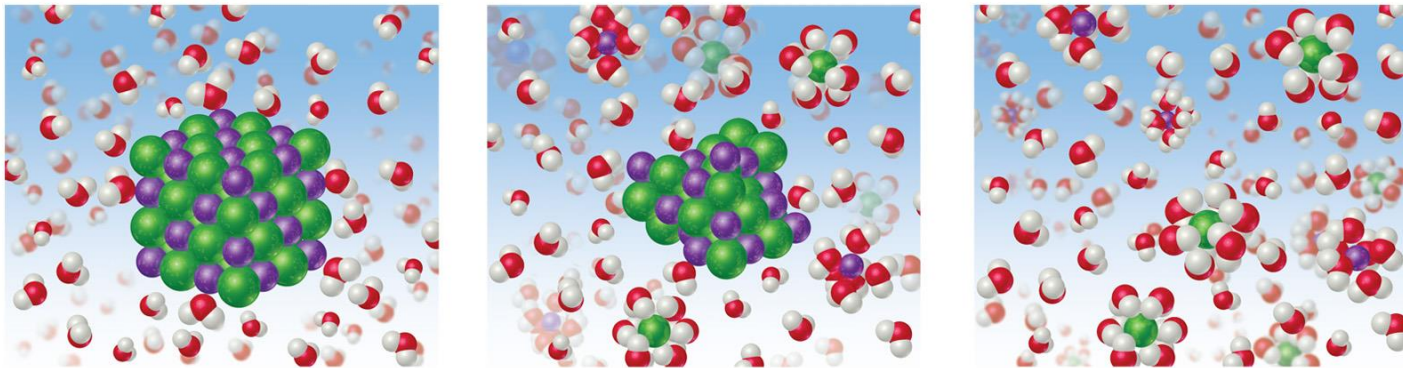How does a solid dissolve into a liquid?

What 'drives' the dissolution process?

What are the energetics of dissolution?

How Does a Solution Form?

1. Solvent molecules attracted to surface ions.
2. Each ion is surrounded by solvent molecules.
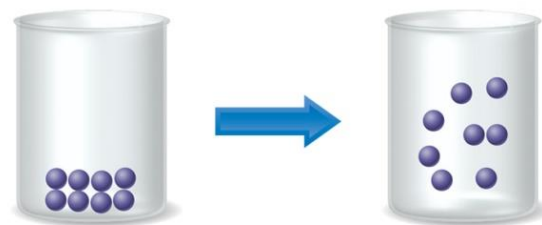3. Enthalpy (DH) changes with each interaction broken or formed.
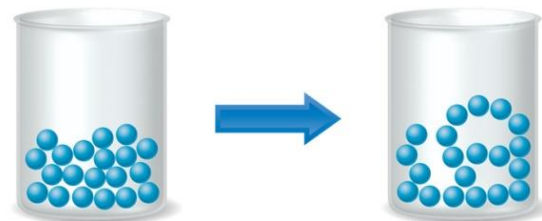
Ionic solid dissolving in water

Energy Changes in Solution

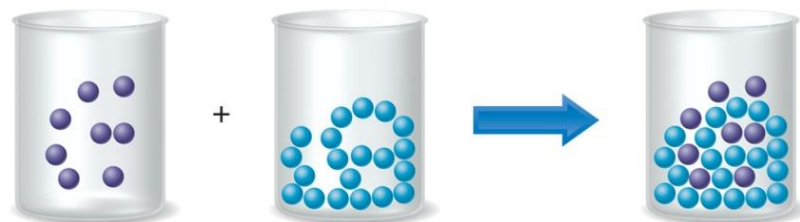To determine the enthalpy change, we divide the process into 3 steps-

1. Separation of solute particles.
2. Separation of solvent particles to make 'holes'.
3. Formation of new interactions between solute and solvent.
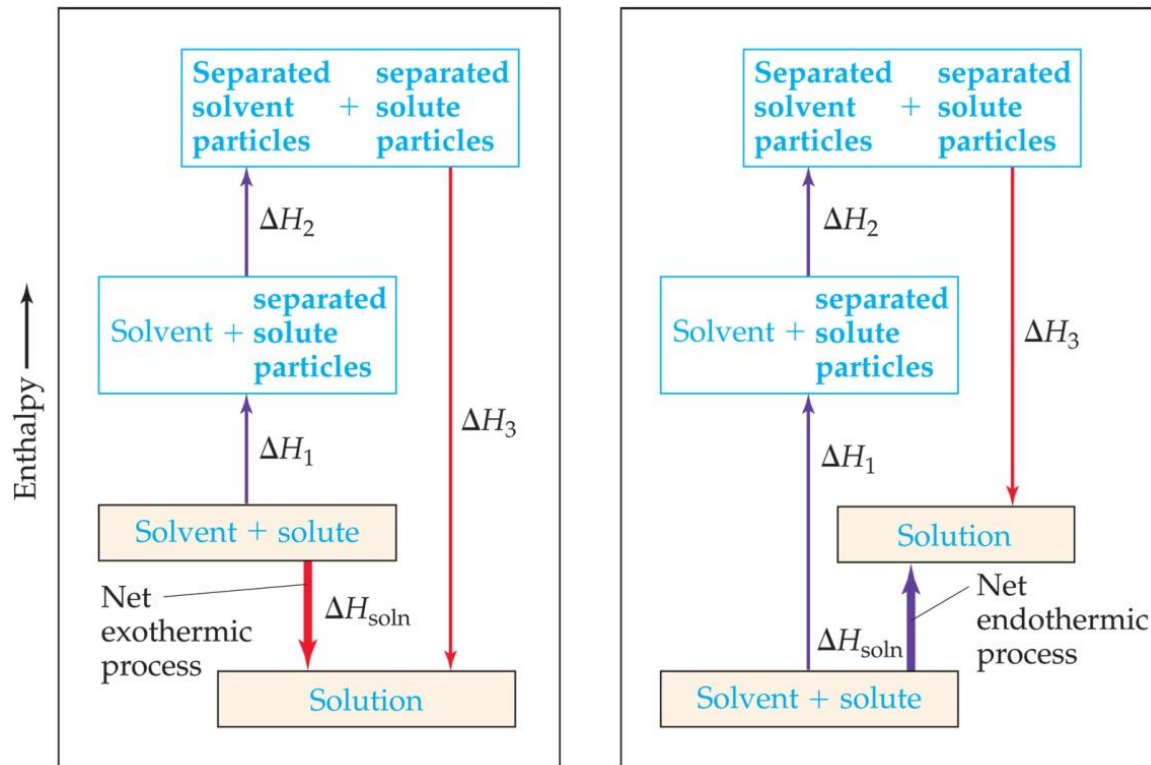
ΔH_1: Separation of solute molecules

ΔH_2: Separation of solvent molecules

ΔH_3: Formation of solute-solvent interactions

Enthalpy changes during dissolution

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

The enthalpy of solution, ΔH_{soln}, can be either positive or negative.

$\Delta H_{soln} (MgSO_4)$ = -91.2 kJ/mol --> exothermic

$\Delta H_{soln} (NH_4NO_3)$ = 26.4 kJ/mol --> endothermic

Why do *endothermic* processes sometimes occur spontaneously?
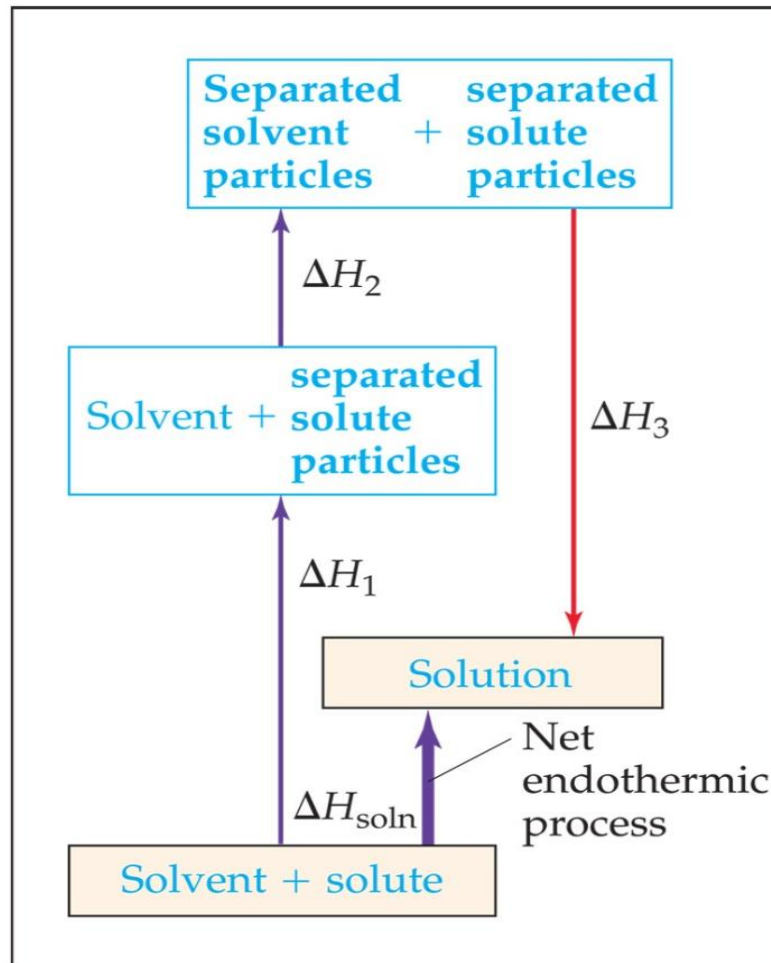
Some processes, like the dissolution of NH_4NO_3 in water, are spontaneous at room temperature even though heat is absorbed, not released.

Colligative Properties

A colligative property may be defined as one which depends on the number of particles in solution and not in any way on the size or chemical nature of the particles. (Greek *colligatus = Collected together*).

Dilute solution containing non volatile solutes exhibit the following properties

➢ Lowering of vapor pressure

➢ Elevation of boiling point

➢ Depression of freezing point

➢ Osmotic pressure

Lowering of vapor pressure

➢ Vapor pressure: The vapor pressure of liquid is the equilibrium pressure of a vapor above it liquid (or solid) that is the pressure of the vapor resulting from evaporation of a liquid (or solid) above a sample of the liquid (or solid) in a closed vessel.

➢ Evaporation: It is the process whereby atoms or molecules in a liquid state (solid state if the substance sublimes) gain sufficient energy to enter the gaseous state. In this process thermal motion of a molecule of liquid must be sufficient to overcome the surface tension and evaporate.

Raults law

For a non volatile solute the relative lowering of the vapour pressure of a dilute solution is equal to the mole fraction of the solute present in dilute solution.

Derivation of Raults law:

The vapour pressure of the solution is,

$$Ps \; \alpha \; \frac{N}{n + N}$$

where n = no of solute & N= no of solvent

$$\text{or } Ps = k\frac{N}{n + N} \quad \text{........(1)}$$

Raults law

In case of pure solvent $n = 0$ and hence

Mole fraction of solvent $= \dfrac{N}{n + N} = \dfrac{N}{0 + N} = 1$

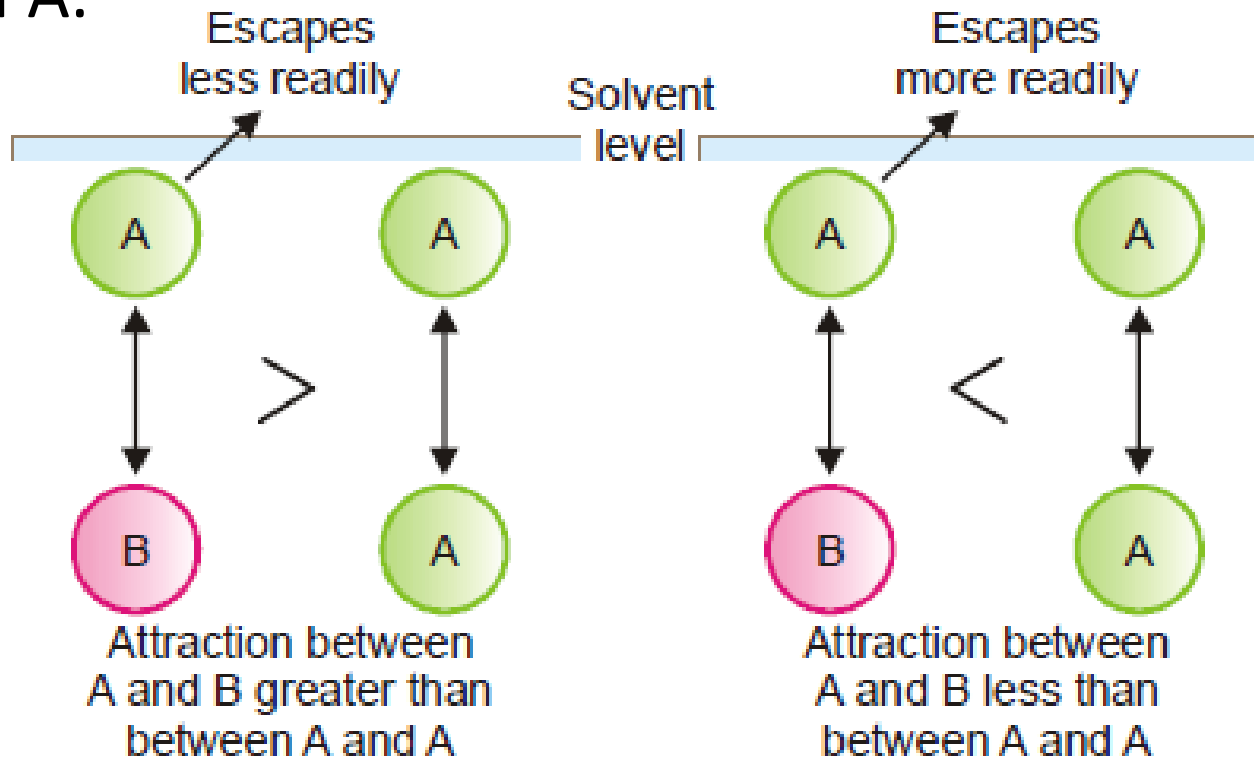From equn (1), P = k

Therefore the equation (1) assumes the form

$Ps = P\dfrac{N}{n + N}$ or, $\dfrac{Ps}{P} = \dfrac{N}{n + N}$ or, $1 - \dfrac{Ps}{P} = 1 - \dfrac{N}{n + N}$

Or, $\dfrac{P - Ps}{P}$ =   n/ n+N

This is the Raults law.

Limitations of Raults law

Suppose the molecules of the solvent and solute are represented by A and B respectively. Now let γ_{AB} be the attractive force between A and B, and γ_{AA} between A and A.

Limitations of Raults law

(1) If $^\gamma AB = {}^\gamma AA$, follow Raoult's law (an ideal solution)

(2) If $^\gamma AB > {}^\gamma AA$ molecule; A will escape less readily (Negative deviation).

(3) On the other hand, if $^\gamma AB < {}^\gamma AA$. Higher vapour pressure (Positive deviation).

(4) In very dilute solutions of non-electrolytes, the solvent and solute molecules are very much alike in both molecular size and molecular attractions. Thus such solutions tend to approach the ideal behaviour and obey Raoult's law fairly accurately.

[solute must be volatile, dilute, not form compounds with solvent & not be dissociated in solvent.]

Determination of molecular mass from vapor pressure lowering

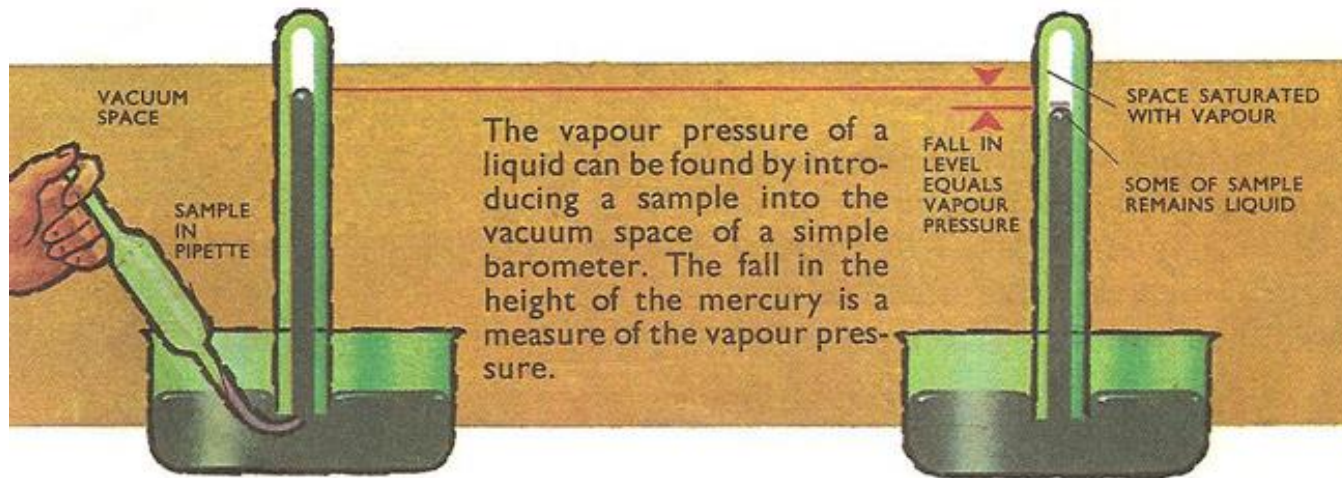$$\frac{P - P_S}{P} = \frac{wM}{mW}$$

Where,

w& W are wt of solute & solvent respectively

m & M are mol mass of solute & solvent.

Mathematical problems

1. Calculate the vapour pressure lowering caused by the addition of 100 g of sucrose (mol mass = 342) to 1000 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg. Solution : P-Ps/P =   n/ n+N (ans).125 mm Hg)

2. The vapour pressure of ether (mol mass = 74) is 442 mm Hg at 293 K. If 3g of a compound A are dissolved in 50 g of ether at this temperature, the vapour pressure falls to 426 mm Hg. Calculate the molecular mass of A. Assume that the solution of A in ether is very dilute. Solution: P-Ps/P = wM/mW (ans 123)

3. A current of dry air was passed through a solution of 2.64 g of benzoic acid in 30.0 g of ether ($C_2H_5OC_2H_5$) and then through pure ether. The loss in weight of the solution was 0.645 g and the ether 0.0345 g. What is the molecular mass of benzoic acid ? Solution :P-Ps/P = w_2/w_1+w_2. (ans 122)

Measurement of vapor pressure lowering

➢ Barometric method

VACUUM SPACE

SAMPLE IN PIPETTE

The vapour pressure of a liquid can be found by introducing a sample into the vacuum space of a simple barometer. The fall in the height of the mercury is a measure of the vapour pressure.

FALL IN LEVEL EQUALS VAPOUR PRESSURE

SPACE SATURATED WITH VAPOUR
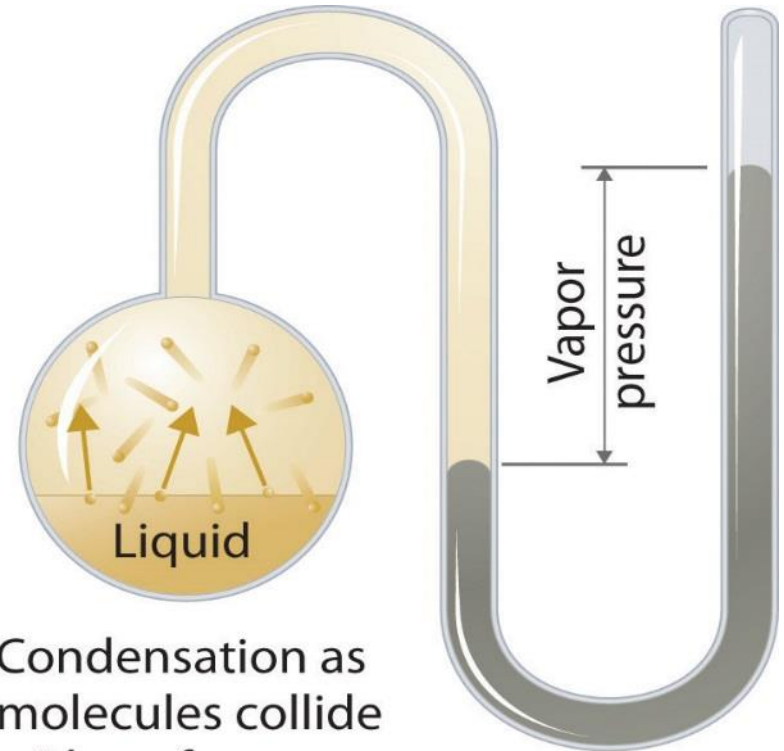
SOME OF SAMPLE REMAINS LIQUID

The vacuum formed when a long tube, closed at one end and filled with mercury, is inverted into a mercury reservoir so that the open end of the tube is below the surface of the mercury. The pressure inside the Torricellian vacuum is the vapour pressure of mercury, about $10-3$ torr.

Manometric method

Vapor pressure
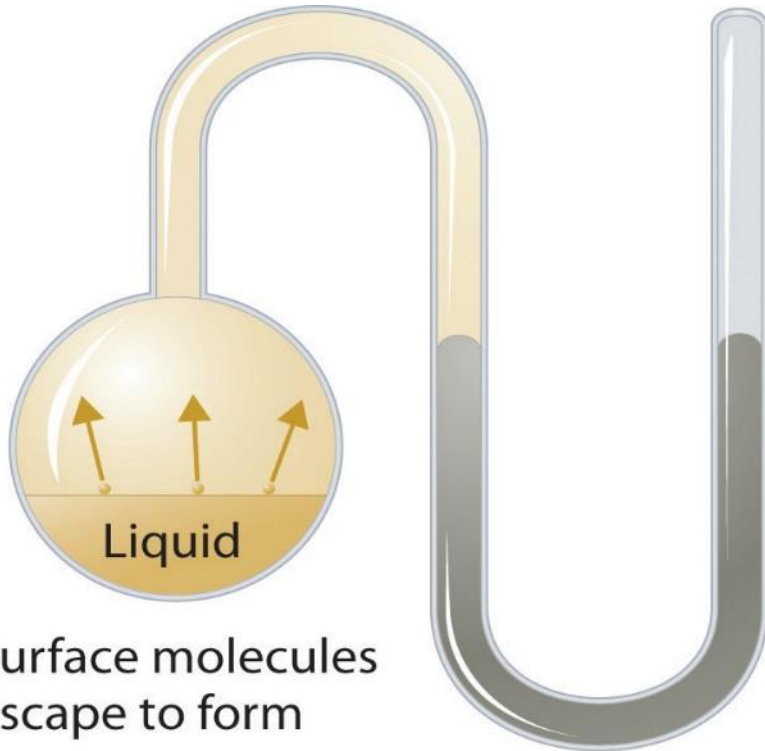
(a) Surface molecules escape to form a vapor

(b) Condensation as molecules collide with surface

Ostwald & walker dynamic method

Dry air →

Solution (Set A)
Loss in weight $\propto p_s$
(W_1)

Solvent (Set B)
Loss in weight $\propto p - p_s$
(W_2)

CaCl$_2$ U-Tube
(If water is used)
Gain in weight $\propto p$
$(W_1 + W_2)$
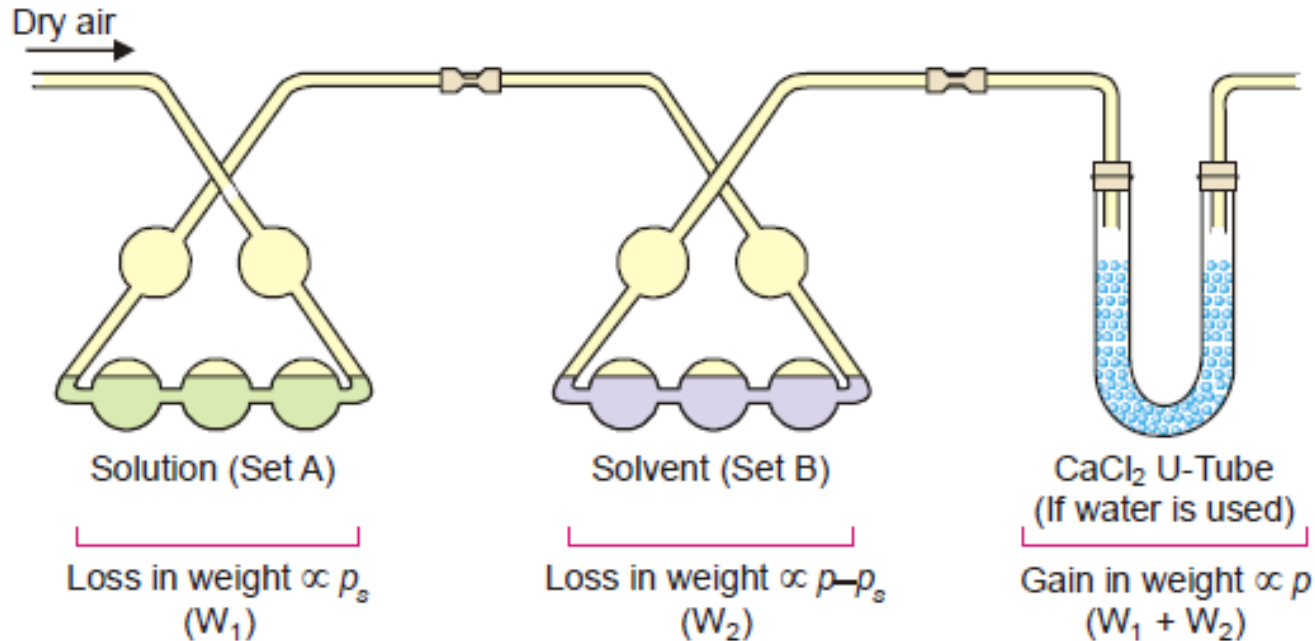
$W_1 \, \alpha \, Ps$ ……………………………………(1)
$W_2 \, \alpha \, P\text{-}Ps$ ………………………………(2)
Adding $W_1 + W_2 \, \alpha \, P$ ………………(3)
Dividing (2) by (3)
$(P\text{-}Ps)/P = W_2/(W_1 + W_2)$ …………(4)

Elevation of boiling point

Relation between boiling point elevation and vapor pressure lowering
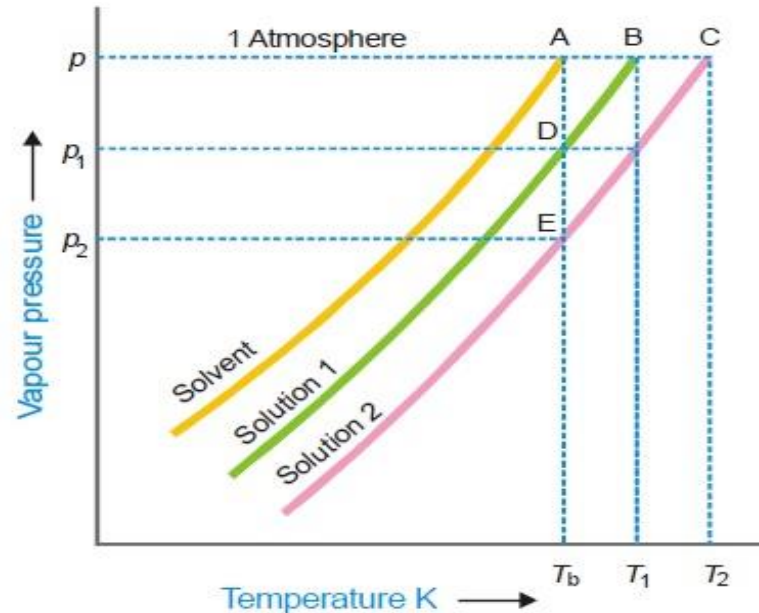
For dilute solutions, the curves BD and CE are parallel and straight lines approximately. Therefore for similar triangles ACE and ABD, we have

$$\frac{AB}{AC} = \frac{AD}{AE}$$

or

$$\frac{T_1 - T_b}{T_2 - T_b} = \frac{p - p_1}{p - p_2}$$

where $p - p_1$ and $p - p_2$ are lowering of vapour pressure for solution 1 and solution 2 respectively. Hence **the elevation of boiling point is directly proportional to the lowering of vapour pressure.**

or $$\Delta T \propto p - p_s \qquad \qquad ...(1)$$

Determination of molecular weight from boiling point elevation

Since p is constant for the same solvent at a fixed temperature, from (1) we can write

$$\Delta T \propto \frac{p - p_s}{p} \qquad \text{...(2)}$$

But from Raoult's Law for dilute solutions,

$$\frac{p - p_s}{p} \propto \frac{wM}{Wm} \qquad \text{...(3)}$$

Since M (mol mass of solvent) is constant, from (3)

$$\frac{p - p_s}{p} \propto \frac{w}{Wm} \qquad \text{...(4)}$$

From (2) and (4)

$$\Delta T \propto \frac{w}{m} \times \frac{1}{W}$$

or

$$\Delta T = K_b \times \frac{w}{m} \times \frac{1}{W} \qquad \text{...(5)}$$

where K_b is a constant called **Boiling point constant or Ebullioscopic constant of molal elevation constant.** If $w/m = 1$, $W = 1$, $K_b = \Delta T$. Thus,
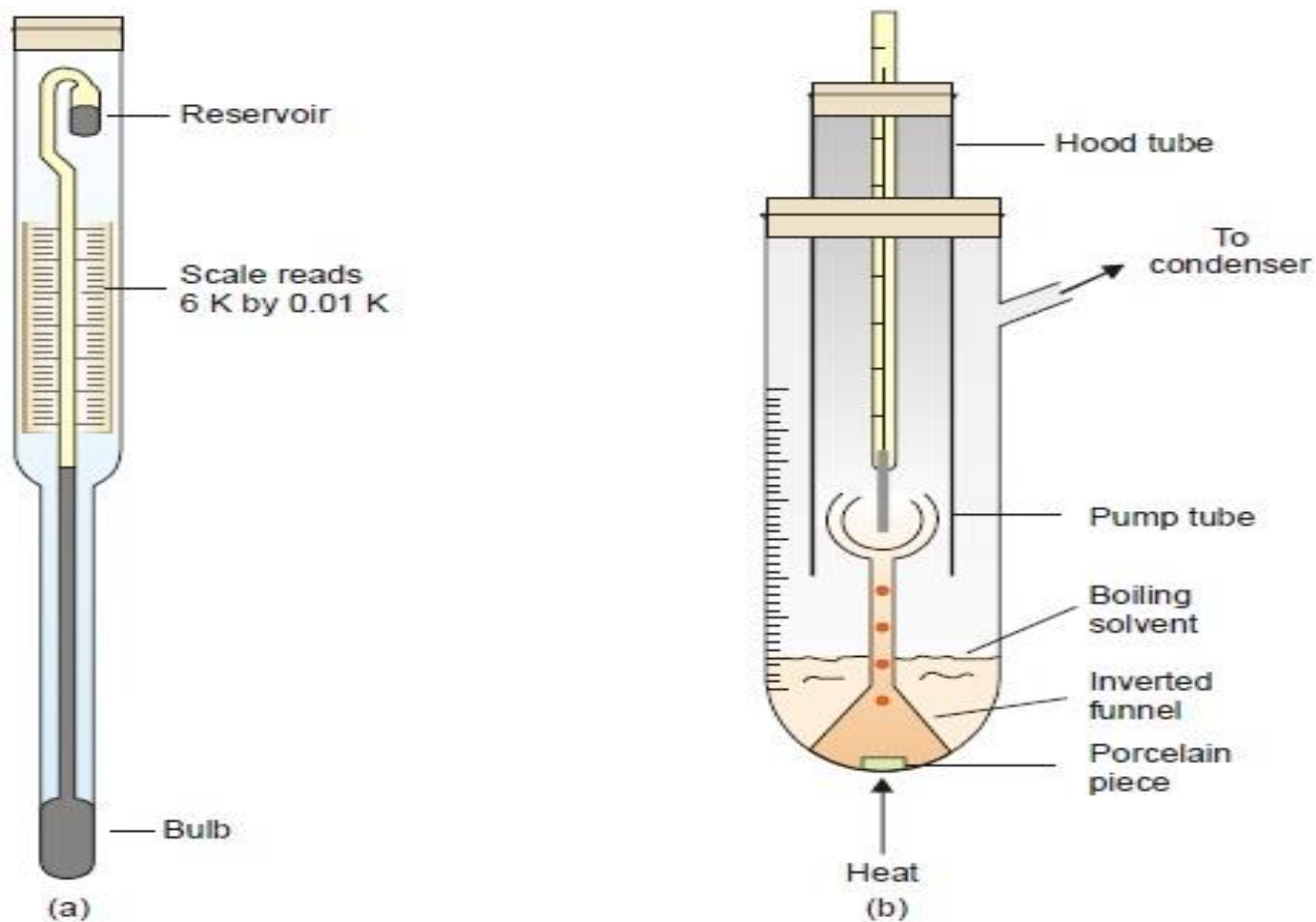
Molal elevation constant may be defined as the boiling-point elevation produced when 1 mole of solute is dissolved in one kg (1000 g) of the solvent.

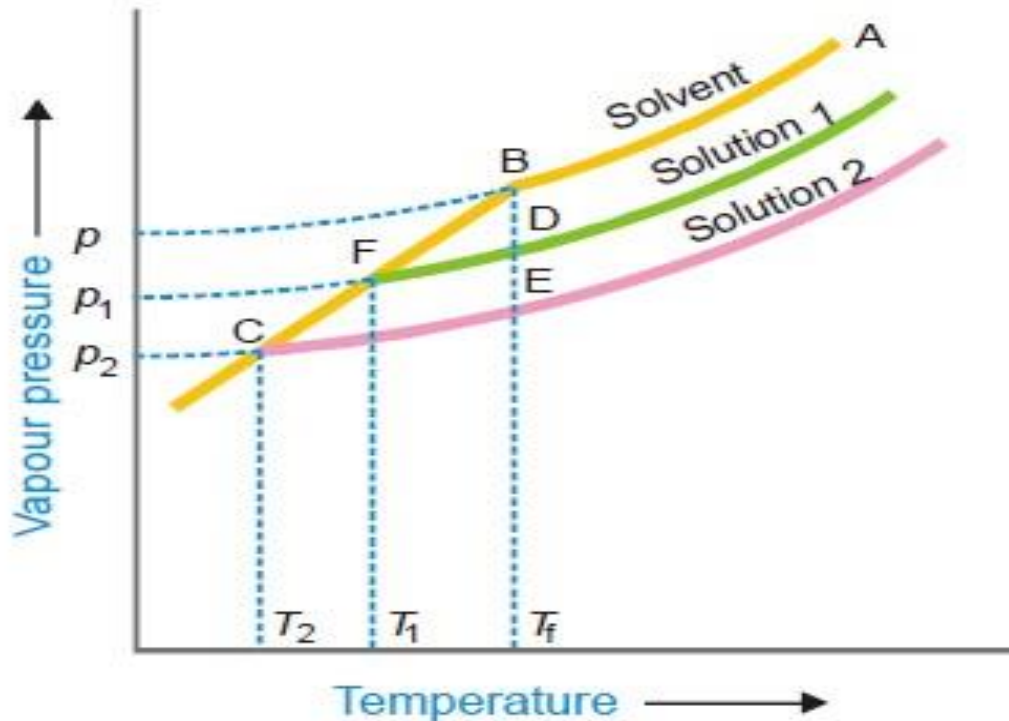# Measurement of elevation of boiling point

➢ Landsberger- Walker method

Cottrell method

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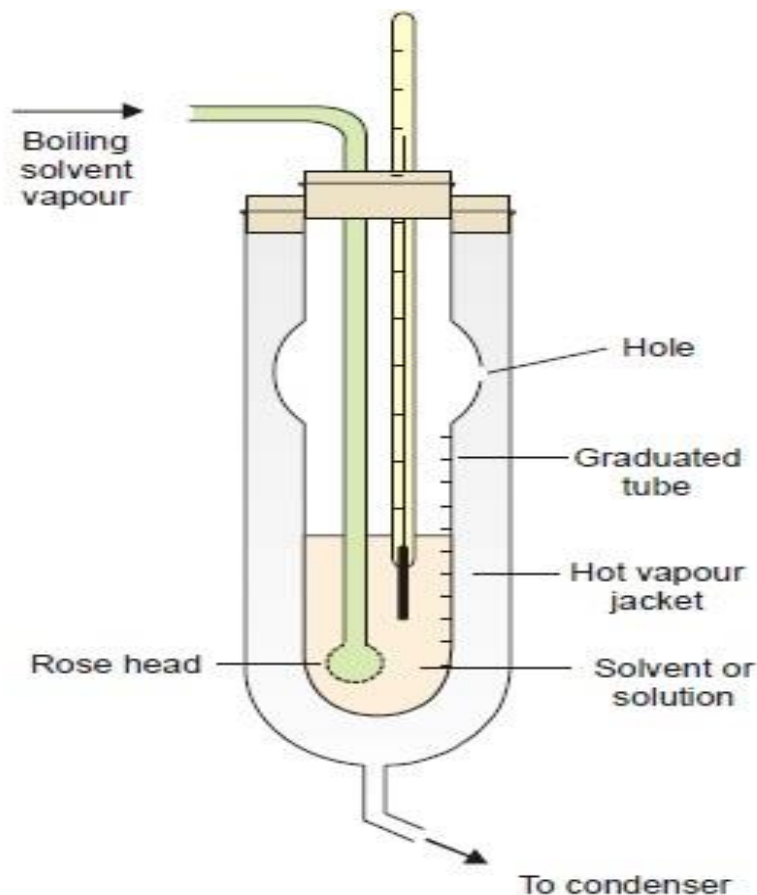
Relation between vapor pressure and depression of freezing point

For dilute solutions FD and CE are approximately parallel straight lines and BC is also a straight line. Since the triangles BDF and BEC are similar,

$$\frac{DF}{EC} = \frac{BD}{BE}$$

or

$$\frac{T_f - T_1}{T_f - T_2} = \frac{p - p_1}{p - p_2}$$

where p_1 and p_2 are vapour pressure of *solution* 1 and *solution* 2 respectively. **Hence depression of freezing point is directly proportional to the lowering of vapour pressure.**

or

$$\Delta T \propto p - p_s \qquad \qquad \qquad \text{...(1)}$$

Determination of Molecular Weight from Depression of Freezing point

Since p is constant for the same solvent at a fixed temperature, from (1) we can write

$$\Delta T \propto \frac{p - p_s}{p} \qquad \qquad \qquad \text{...(2)}$$

But from Raoult's Law for dilute solutions,

$$\frac{p - p_s}{p} = \frac{wM}{Wm} \qquad \qquad \qquad \text{...(3)}$$

Since M (mol wt) of solvent is constant, from (3)

$$\frac{p - p_s}{p} = \frac{w}{Wm} \qquad \qquad \qquad \text{...(4)}$$

from (2) and (4)

$$\Delta T \propto K_f \times \frac{w}{m} \times \frac{1}{W}$$

or

$$\Delta T = K_f \times \frac{w}{m} \times \frac{1}{W} \qquad \qquad \qquad \text{...(5)}$$

where K_f is a constant called **Freezing-point constant or Cryoscopic constant or Molal depression constant.** If $w/m = 1$ and $W = 1$, $K_f = \Delta T$. Thus,
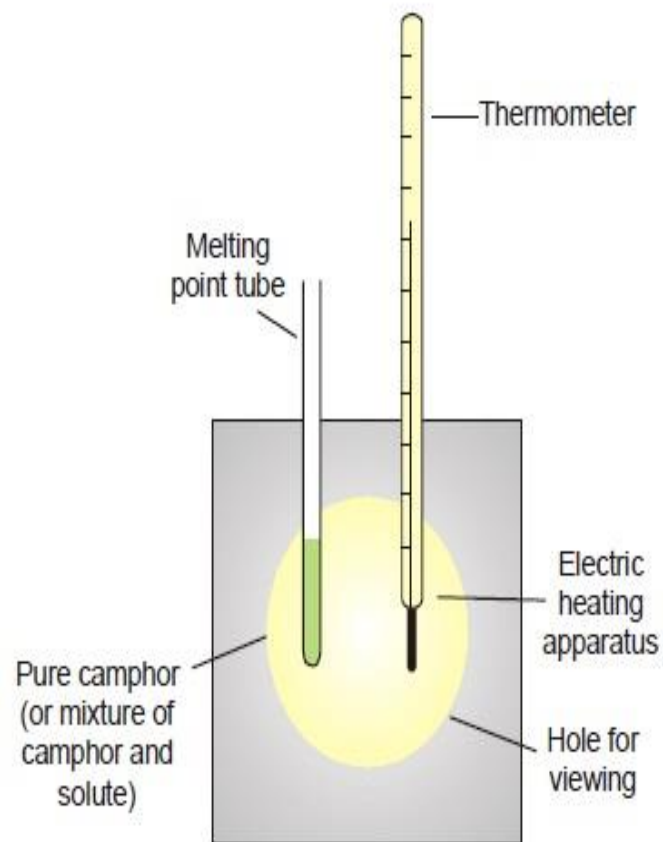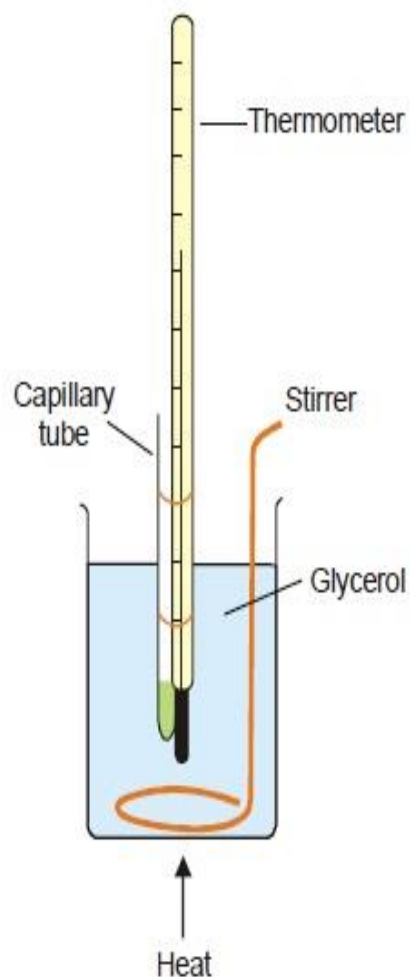
Molal depression constant may be defined as the freezing-point depression produced when 1 mole of solute is dissolved in one kg (1000 g) of the solvent.

Measurement of depression of freezing point

➢ Beckmann's method

# Rast Camphor method

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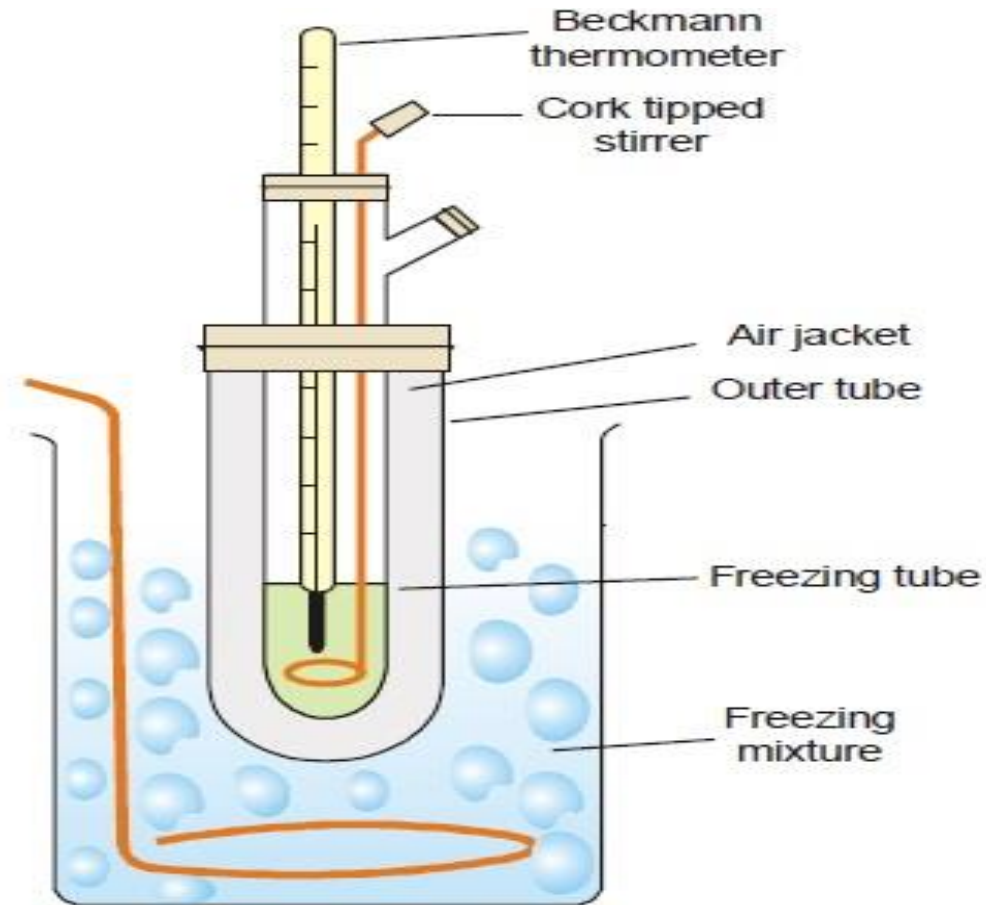
Problems and solutions

➢ Acetone boils at 56.38°C and a solution of 1.41 grams of an organic solid in 20 grams of acetone boils at 56.88°C. If K for acetone per 100 g is 16.7, calculate the mass of one mole of the organic solid. (m=1000*Kb*w/T*W, ans 235)

➢ 0.440 g of a substance dissolved in 22.2 g of benzene lowered the freezing point of benzene by 0.567°C. Calculate the molecular mass of the substance. (Kf = 5.12°C mol−1) (m=1000*Kf*w/T*W, ans 178.9)

Osmotic pressure

➤ The flow of the solvent through a semi-permeable membrane from pure solvent to solution, or from a dilute solution to concentrated solution, is termed Osmosis (Greek *Osmos = to push).*

➤ The hydrostatic pressure built up on the solution which just stops the osmosis of pure solvent into the solution through a semi-permeable membrane, is called Osmotic Pressure.

➤ Osmotic pressure may be defined as the external pressure applied to the solution in order to stop the osmosis of solvent into solution separated by a semi-permeable membrane.
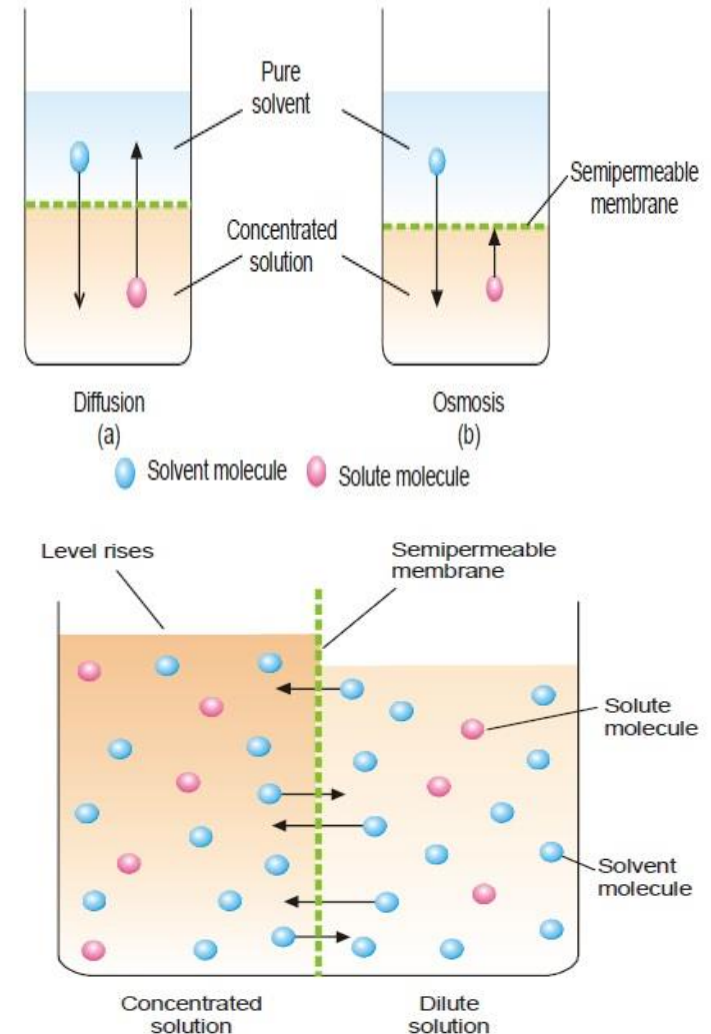
Laws of osmotic pressure

- Boyle – Vant hoff law for solution, $\pi \, \alpha \, 1/V$…….(1)
- Charles Vant hoff law for solution, $\pi \, \alpha \, T$…………..(2)

$$\text{so, } \pi \, \alpha \, T/V$$

$$\pi = RT/V$$

$$\pi V = RT \text{ where, } R = \text{gas constant}$$
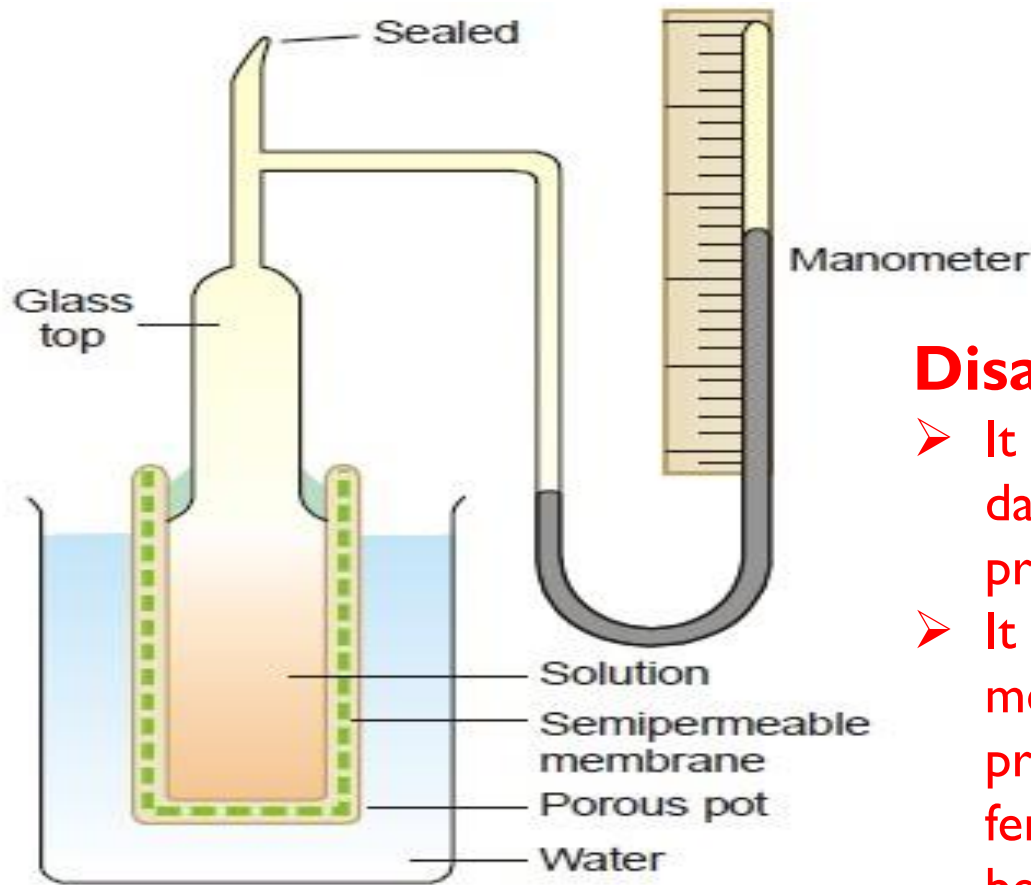
For n mole, $\quad \pi V = nRT$

$$\pi V = wRT/M$$

$$M = wRT/\pi V$$

(molecular weight from osmotic pressure)

Relation between osmotic pressure and vapor pressure lowering:
$P - P_s \, \alpha \, \pi$
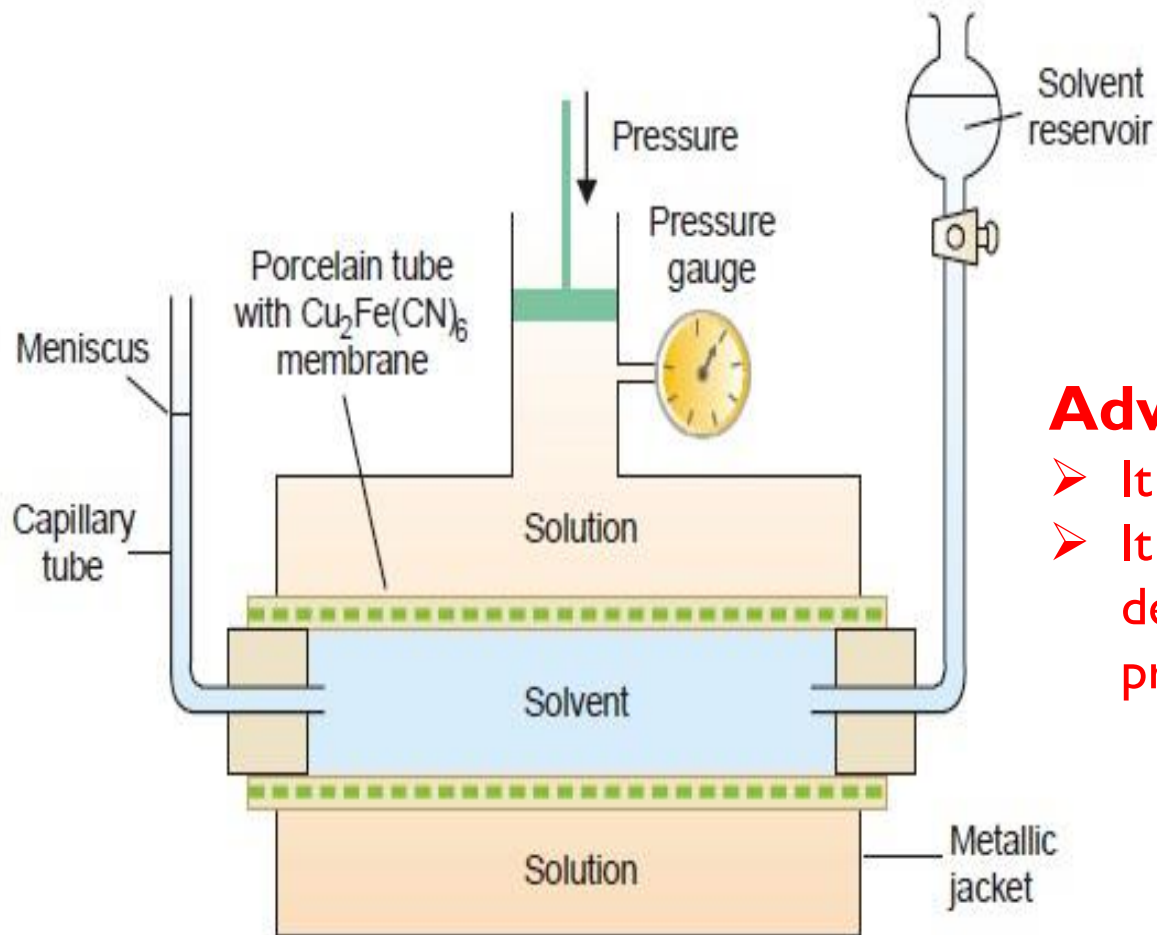
Measurement of osmotic pressure

➢ Pfeffers method

Disadvantages-
- ➢ It is slow and it takes a few days before the highest pressure is reached.
- ➢ It cannot be used for measuring high osmotic pressures as the ferrocyanide membrane being weak ruptures.
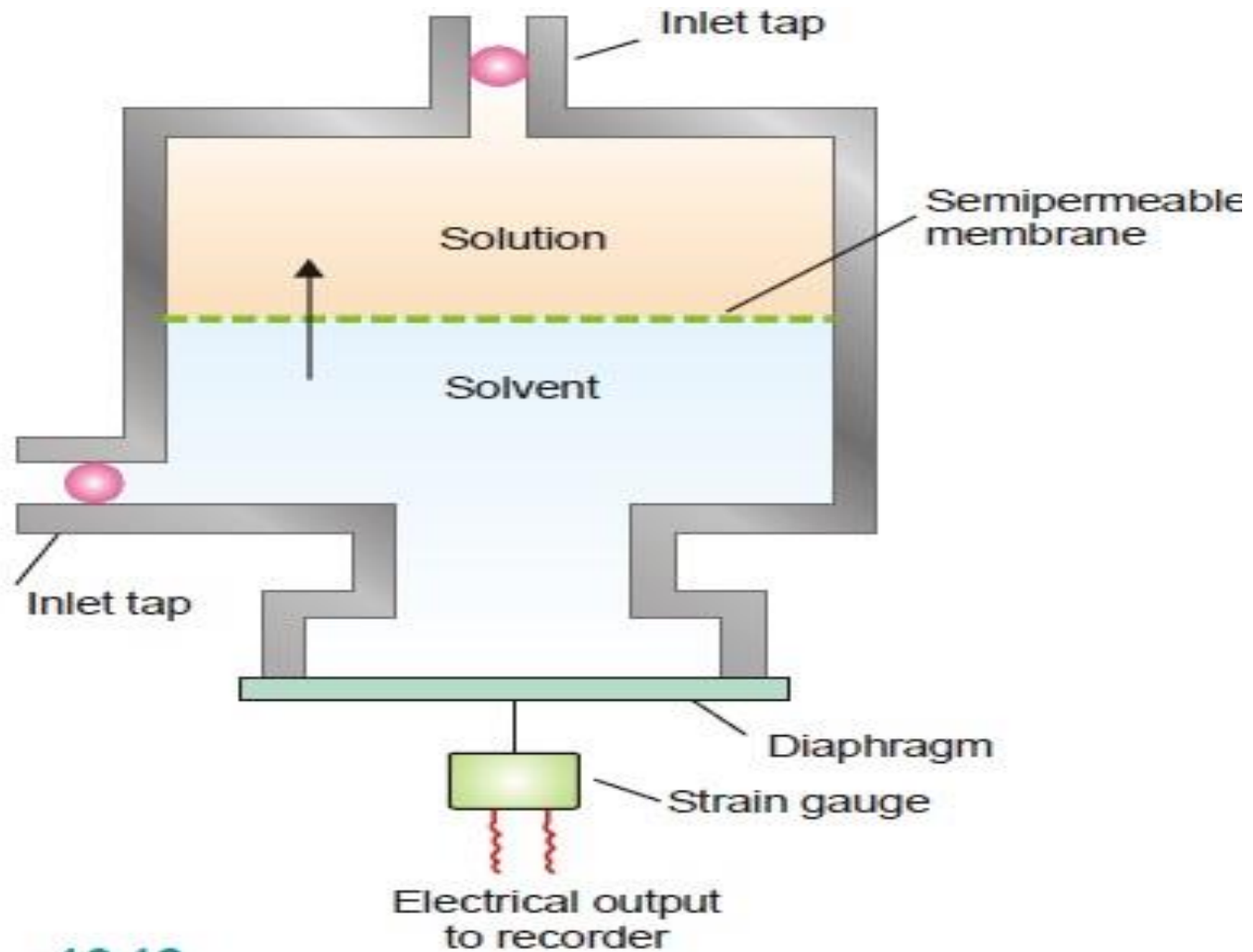
Barkley and Hartly method

Advantages-
- It is quick and accurate.
- It can be used for determining high osmotic pressures.

A modern Osmometer

Colligative properties of electrolytes

➤ The colligative properties depend solely on the total number of solute particles present in solution. The various electrolytes ionize and yield more that one particle per formula unit in solution. Therefore, the colligative effect of an electrolyte solution is always greater than that of a nonelectrolyte of the same molal concentration.

➤ To represent the colligative properties of electrolytes, van't Hoff (1880) suggested a factor I which is defined as : the ratio of the colligative effect produced by an electrolyte solution to the corresponding effect for the same concentration of a nonelectrolyte solution.

$$i = \frac{\Delta T_f}{[\Delta T_f]_0} = \frac{\Delta T_b}{[\Delta T_b]_0} = \frac{\Delta p}{[\Delta p]_0}$$

$$= \frac{\pi}{[\pi]_0}$$

$$i = \frac{\text{Actual number of particles}}{\text{Number of particles for no ionization}}$$