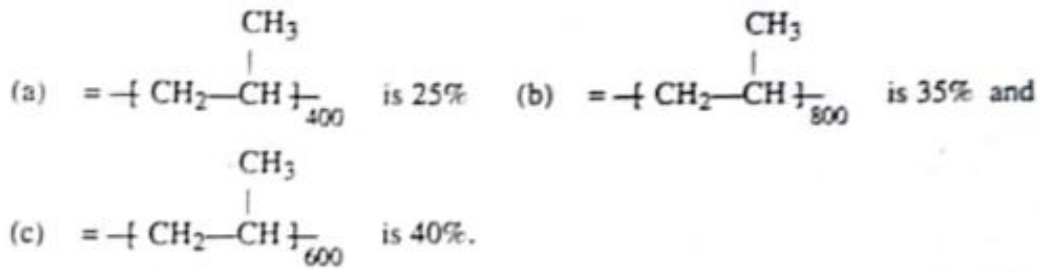


**Problem 9.** Calculate the number average and weight average molecular masses of polypropylene polymer with the following composition :



**Solution :** Molecular mass of (a) =  $[(12 \times 3) + (6 \times 1)] \times 400 \Rightarrow M_1 = 42 \times 400 = 16800$   
 Molecular mass of (b) =  $42 \times 800 \Rightarrow M_2 = 33600$   
 Molecular mass of (c) =  $42 \times 600 \Rightarrow M_3 = 25200$   
 As  $n_1 = 25$ ,  $n_2 = 35$  and  $n_3 = 40$

Thus 
$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3}$$

$$= \frac{(25 \times 16800) + (35 \times 33600) + (40 \times 25200)}{25 + 35 + 40}$$

$$= \frac{2604000}{100} = 26040$$

And 
$$\bar{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2}{n_1 M_1 + n_2 M_2 + n_3 M_3}$$

$$= \frac{(7.056 \times 10^9) + (3.951 \times 10^{10}) + (2.540 \times 10^{10})}{2604000}$$

$$= \frac{7.1966 \times 10^{10}}{2604000}$$

$$= 27637$$

*Handwritten notes:*  
 1.20  
 1.10  
 1.00

**2.2. POLYDISPERSITY AND MOLECULAR WEIGHT DISTRIBUTION IN POLYMERS**

A polymer is composed of a large number of monomer units and any polymer sample contains molecules of different chain lengths. This heterogeneity of the polymer sample is called its polydispersity

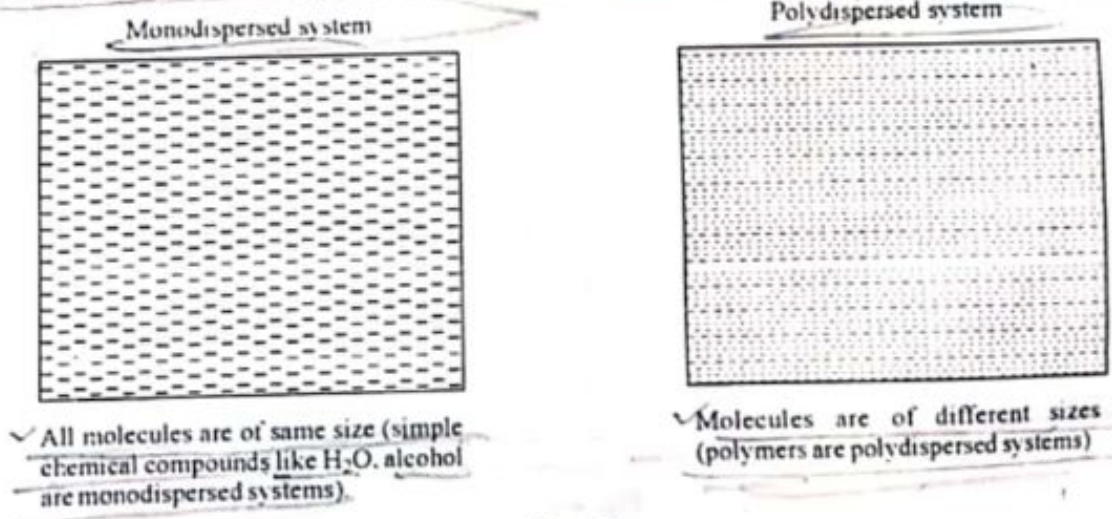


Fig. 2.1

as opposed to a monodispersed sample in which all the chains are identical chemically as well in size. The weight average molecular weight  $\bar{M}_w$  is always larger than the number average molecular weight  $\bar{M}_n$ , unless the sample is monodispersed, in which case  $\bar{M}_w = \bar{M}_n$ . The ratio  $\bar{M}_w/\bar{M}_n$  is called the polydispersity index (P.D.I) of a polymer sample.

The polydispersity co-relates with the concept of 'average' molecular weight but it does not co-relate with the dispersity pattern of the polymer sample. For example, 40,000 is the average molecular weight of the polymer sample. It means that the value of molecular weights of molecules ranging from 20,000 to 80,000 or from 500 to 100,000, the figure is uncertain. Therefore two polymer samples of the same 40,000 average molecular weight have similar properties in some respect while different in other respect. Thus it is necessary to know both the average molecular weight and the dispersion pattern of the given polymer sample. This dispersity can be expressed by a simple molecular weight distribution curve with respect to the lowest to the highest molecular weight. Such a curve for a polymer sample is plotted between the number of molecules ( $n_i$ ) of a particular molar mass ( $M_i$ ) and their corresponding molecular weight. (The curve shows the relative positions of the various average molecular weights in a polydispersed polymer sample. Here  $\bar{M}_w > \bar{M}_n$  and that  $\bar{M}_v$  is closer to  $\bar{M}_w$  than to  $\bar{M}_n$ .)

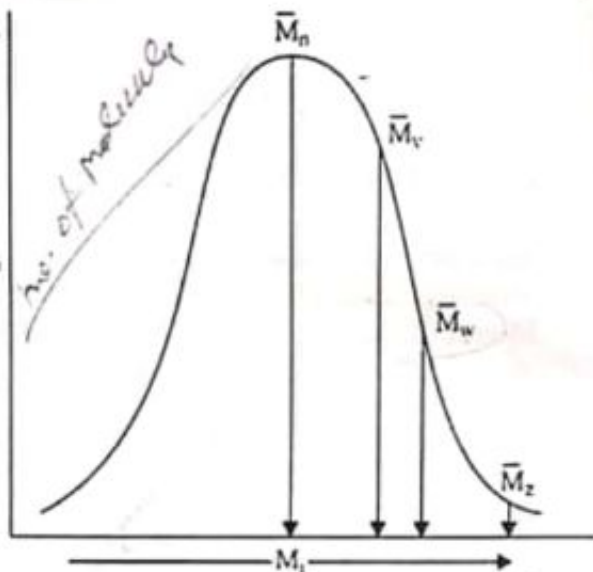


Fig. 2.2

*particular molar mass (M<sub>i</sub>)*

Polydispersity is a very important parameter. It gives an idea of the lowest and the highest molecular weight species as well as the distribution pattern of the intermediate molecular weight species. It arises due to variation in the degree of polymerisation attained by different molecules during the polymerisation process and polymers obtained by different polymerisation techniques show different polydispersities.

The figure (2.3) shows molecular mass distribution in two polymer samples have the same number-average molecular weight but different polydispersities. Sample 1 has a narrower dispersion pattern and hence, a lower polydispersity than sample 2.

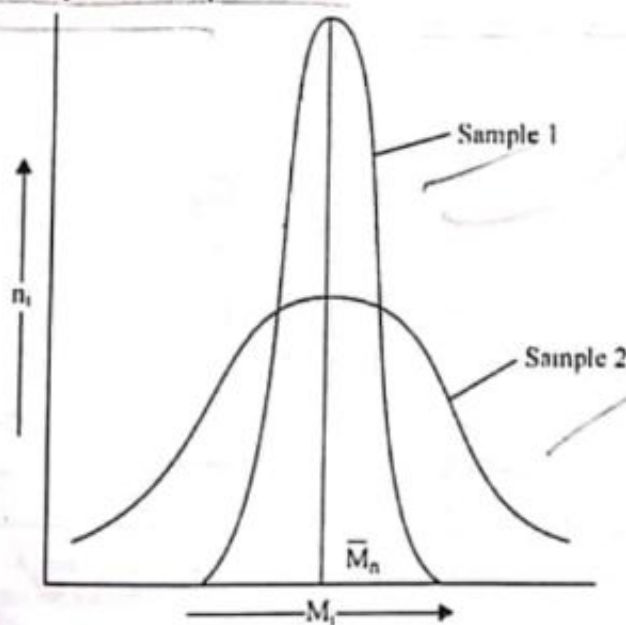


Fig. 2.3

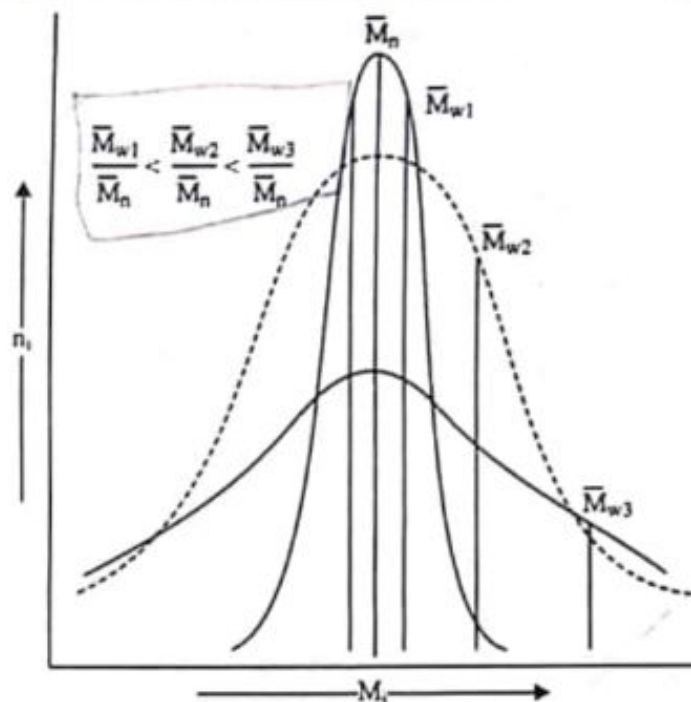


Fig. 2.4

contains a known groups to

Yet there is another way to look into the polydispersities of polymer sample.

For all synthetic polymers  $\frac{\bar{M}_w}{\bar{M}_n}$  is higher than 1.

As the molecular weight distribution becomes broader that is, as the dispersity increases, the value of  $\bar{M}_w/\bar{M}_n$  increases.

### 2.3. THE PRACTICAL SIGNIFICANCE OF POLYMER MOLECULAR WEIGHT

Many commercially useful polymers are selected on the basis of their physical properties such as melt viscosity, impact strength or tensile strength. These properties are dependent on the molecular weight of the polymer or its degree of polymerisation. For example, melt viscosity increases with molecular weight. But at very high molecular weight, it rises more steeply than at low molecular weights.

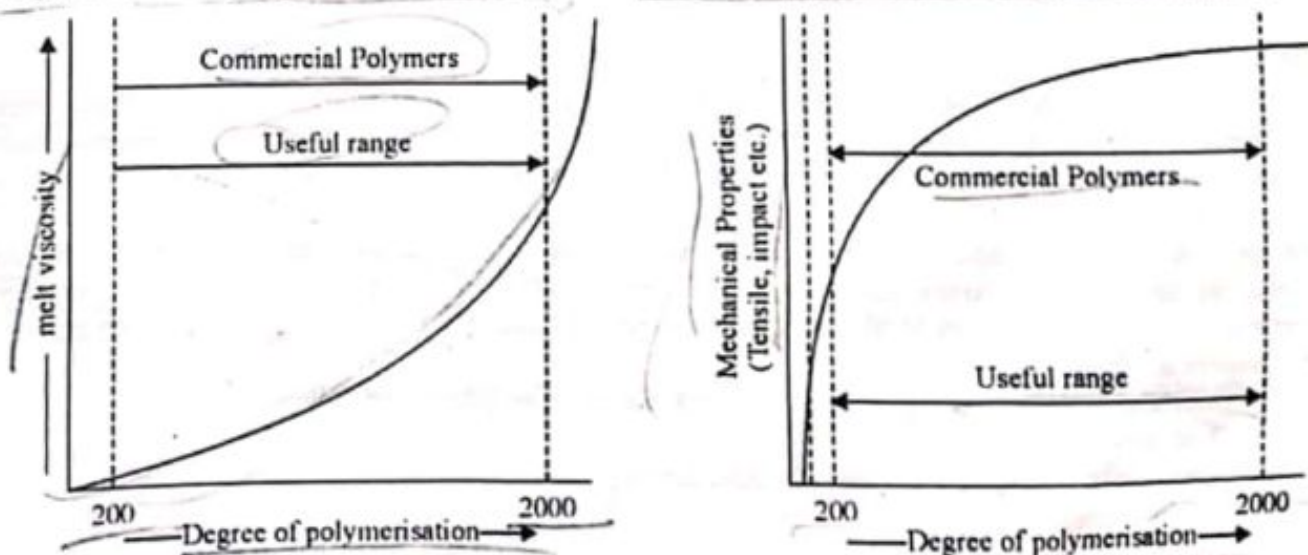


Fig. 2.5

A commercially useful polymer should have a low melt viscosity to permit ease of processing, but, at the same time should show good strength.

The tensile and impact strengths also increase with molecular weight.

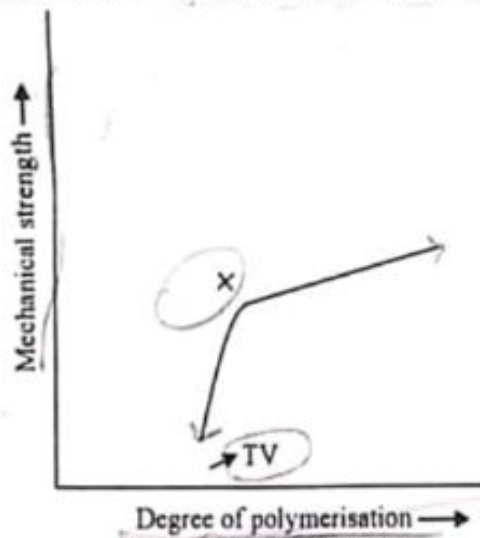


Fig. 2.6

When a graph is plotted showing change of mechanical strength against degree of polymerisation (DP), it comes as shown in the figure (2.6). Qualitatively, the nature of the curve is more or less the same for all polymers. Every polymer has a threshold value (TV) for its degree of polymerisation. This value varies from one polymer to another. Below this value polymer does not possess any strength, and exists as friable powder or as liquid resin.

At certain DP value (shown as X on the graph) the polymer attains more or less full strength. This value also varies from one polymer to another. For example :

Polymer	Threshold DP value	DP value of point (X)
Cellulose	60	250
Vinyl polymers	100	400

It has been found that polymers do not show strength for DP values of lower than 30 and the optimum strength of the most of the polymers is obtained at DP value of around 600. The useful range of DP is from 200 to 2000.

## 2.4. MEASUREMENT OF MOLECULAR WEIGHT

### Introduction

There are various physical and chemical methods for measurement of molecular weight of polymers. These methods are functional-group analysis, measurement of colligative properties (osmometry), light scattering or ultra centrifugation or measurement of dilute solution viscosity. All these methods are absolute except dilute-solution viscosity method. By these methods molecular weight can be calculated directly. Dilute solution viscosity method (viscometry) however, is not a direct measure of molecular weight. All molecular weight methods require solubility of polymer and all involve extrapolation to infinite dilution or operation in a solvent in which ideal solution behaviour is attained (But some types of end group analysis do not require all these).

The methods used for molecular weight determination of polymers are follows :

- End-group analysis.
- Colligative property measurement (Osmometry).
- Light scattering.
- Ultracentrifugation.
- Viscometry.

### 2.4.1. End-Group Analysis

Molecular weight determination through group analysis requires that the polymer contains a known number of determinable groups per molecule. The long-chain nature of polymers limits such groups to end groups. Thus the method is called end-group analysis. Since methods of end-group analysis count the number of molecules in a given weight of sample, they give the number-average molecular weight of the polymer ( $M_n$ ).

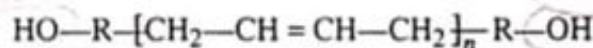
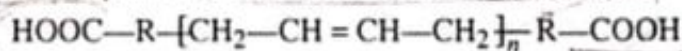
The method is not so useful at high molecular weight (above 25,000), as the fraction of end groups becomes too small to be measured with accuracy.

In this method, first, the total number of functional groups [-OH, -COOH, -CHO, -NH<sub>2</sub>, OCOR etc.] present in a given weight of the sample is determined by usual chemical methods.

This is expressed as functional group equivalent/100 gm. From a knowledge of the functional group equivalent and the functionality, the number average molecular weight can be calculated using the equation :

$$\bar{M}_n = \frac{\text{functionality}}{\text{functional group equivalent}}$$

Functionality is defined as the number of reactive functional groups present in each macromolecule. Thus, the functionality of carboxyl-terminated and hydroxyl-terminated polybutadienes (CTPB and HTPB) is two, as each molecule possesses two reactive functional groups :



Functionality = 2

The procedure is as follows :

An accurately weighed quantity (less than 1 gm) of, for example CTPB sample is dissolved in the ethanol-toluene (1 : 3) mixture. This is titrated against a 0.1 N alcoholic potassium hydroxide solution using phenolphthalein as an indicator. The end point is the appearance of a slightly pink colour. Then,

$$\text{Carboxyl value} = \frac{VN(56.1)}{W} \text{ mg of KOH/gm}$$

where V = Volume of KOH consumed in ml.,

N = Normality of KOH solution.

W<sub>gm</sub> = Weight of the sample taken.

$$\text{Carboxyl equivalent / 100 gm} = \frac{VN(56.1)}{W(1000)} \times \frac{100}{56.1} = \frac{VN}{10W}$$

In a particular experiment, if 0.8734 gm of the sample has consumed 5.1 ml of 0.1242 N alcoholic KOH solution, then

$$\begin{aligned} \text{Carboxyl equivalent/100 gm} &= \frac{5.1 \times 0.1242}{10 \times 0.8734} \\ &= 0.0725 \end{aligned}$$

Assuming a functionality of 2, we get

$$\bar{M}_n = \frac{2 \times 100}{0.0725} = 2760$$

This method is valuable for linear polymer molecules having determinable end groups and for those obtained by a known polymerisation mechanism without side reactions. This is because side reactions during polymerisation (such as branching or chain transfer) may introduce errors in the assumed functionality and hence, lead to erroneous results.

The chemical methods are often limited by insolubility of the polymer in solvents suitable for the titrations.

### 2.4.2. Colligative Property Measurement (Osmometry)

The colligative property methods are based on vapour-pressure lowering, boiling point elevation (ebulliometry), freezing point depression (cryoscopy) and the osmotic pressure (osmometry). The colligative properties and molecular weight for infinitely dilute solutions are related to each other. The activity of the solute in a solution becomes equal to its mole fraction as the solute concentration becomes sufficiently small. The activity of the solvent must equal its mole fraction under these conditions. The depression of the activity of the solvent by a solute is equal to the mole fraction of the solute.

The following equations are used for polymer solutions to determine the number average molecular weight ( $M_n$ ).

$$\lim_{C \rightarrow 0} \frac{\Delta T_b}{C} = \frac{RT^2}{\rho \Delta H_v} \cdot \frac{1}{M_n}$$

$$\lim_{C \rightarrow 0} \frac{\Delta T_f}{C} = \frac{RT^2}{\rho \Delta H_f} \cdot \frac{1}{M_n}$$

$$\lim_{C \rightarrow 0} \frac{\pi}{C} = \frac{RT}{M_n}$$

where  $\Delta T_b$ ,  $\Delta T_f$  and  $\pi$  are the boiling point elevation, freezing point depression, and osmotic pressure, respectively.  $\rho$  is the density of the solvent;  $\Delta H_v$  and  $\Delta H_f$  are the enthalpies of vapourization and fusion, respectively of the solvent per gram and  $C$  is the solute concentration in gms/ml.

The osmotic pressure technique is more useful for polymer solutions than other colligative techniques. There are two types of osmotic pressure methods.

- Vapour-phase osmometry
- Membrane osmometry.

#### (a) Vapour-Phase Osmometry :

**Principle :** Vapour phase osmometry is an indirect measurement of vapour-pressure lowering. This method is used for measuring  $M_n$  of polymer sample. The method is based on the principle that at a given temperature the vapour pressure of a solution is less than that of the pure solvent. Now a drop each of a pure solvent and the solution is kept in an atmosphere saturated with the solvent vapour. Since the vapour pressure of the solution is lower than that of the pure solvent, condensation of the solvent takes place from the saturated vapour phase on to the solution droplet. The solution droplet, therefore, starts getting diluted as well as heated up by the latent heat of condensation of the solvent condensing on it. Due to the temperature rise and increased concentration of the solvent, the vapour pressure of the solution droplet increases. The process of condensation and the temperature rise continues till the vapour pressure of the solution droplet becomes equal to that of the pure solvent. The total rise in temperature  $\Delta T$ , will be proportional to the mole fraction of the solute,  $n$ , in the solution.

$$\Delta T = \frac{RT^2 n}{\Delta H_v}$$

where  $\Delta H_v$  is the heat of vapourisation.

The apparatus used for this method is called as "vapour-pressure osmometer (VPO)". The solution and the solvent droplet are placed directly on two thermistors in a wheatstone bridge circuit in such a way that the temperature rise can be measured very accurately as a function of output voltage  $\Delta V$ .  $\Delta V$  is related to the molecular weight of the solute (polymer) by the equation :

$$\frac{\Delta V}{C} = \frac{K}{M_n} + KBC$$

where  $K$  is the calibration constant.

**Instrumentation :**

A solvent vessel made of glass is placed in an aluminium block. This aluminium block is closed by a stainless steel lid through a Teflon gasket. This vessel provides the space for the atmosphere of solvent vapour wherein the transistors are suspended. The stainless steel lid is covered by another metal block through which several syringes for placing the solution and solvent drops on the thermistors are introduced. The entire assembly is thermostated to maintain a constant temperature.

**Method :** First, the solvent is added to the solvent vessel through a syringe and solvent drops are also placed on each thermistor. Since there will not be any condensation on either of the thermistors, there is obviously no temperature difference and hence, the instrument should read zero. In the next step, the instrument is calibrated with a standard sample of a known molecular weight. Its four to five solutions of known concentrations are prepared. A drop of the solution of one particular concentration is placed on a thermistor. Now, the solvent starts condensing on the solution droplet and the rise in temperature occurs which is directly measured as the bridge imbalance output value  $\Delta v$ . The process is repeated with solutions of different concentrations and  $\Delta V$  values for each concentration are noted.

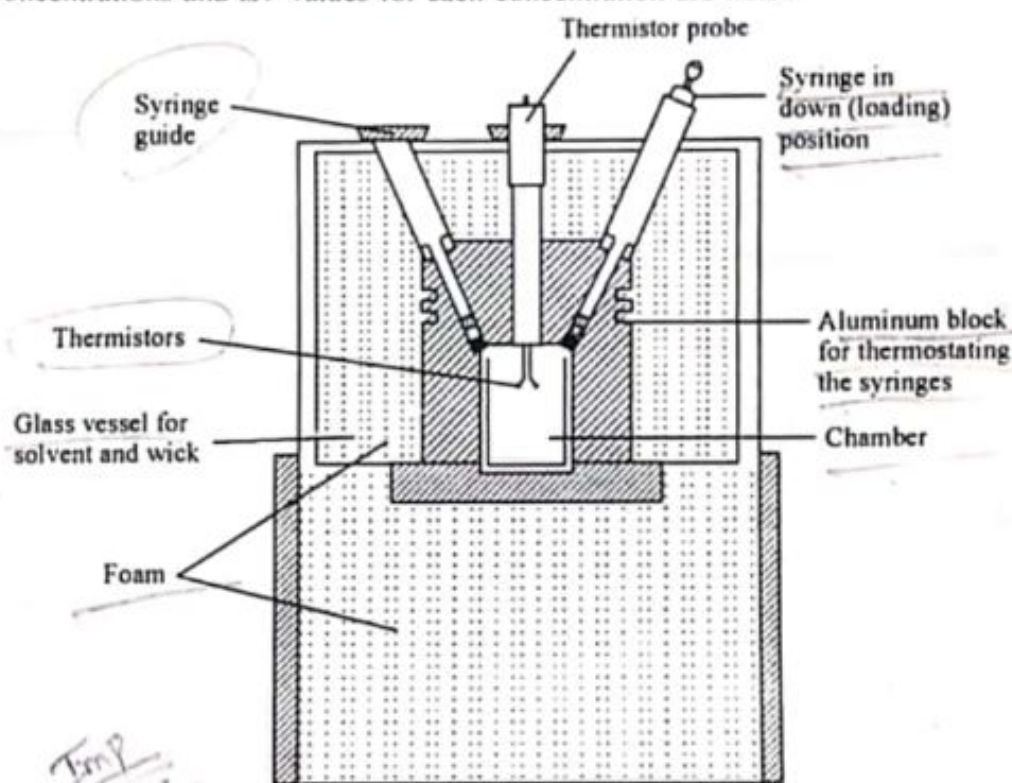


Fig. 2.7. Measurement chamber of vapour phase osmometer

A graph of  $\Delta V/C$  versus  $C$  is plotted and extrapolated to zero concentration. The ordinate intercept will then be  $(\Delta V/C)_{C \rightarrow 0}$ .  $K$  can be calculated by using the equation,

$$K = M \cdot (\Delta V/C)_{C \rightarrow 0}$$

where  $M$  is the molecular weight of the standard sample.

The molecular weight of the unknown sample can be calculated by repeating the same procedure with the same solvent. By knowing the ordinate intercept  $(\Delta V/C)_{C \rightarrow 0}$  the molecular weight of the unknown sample will be given by

$$\bar{M}_n = \frac{K}{(\Delta V/C)_{C \rightarrow 0}}$$

### (b) Membrane Osmometry :

This technique is used to determine the number-average molecular weight of polymers. It is based on the phenomenon of osmosis. But it is not a useful technique for studying solutes of low molar mass, because it is difficult to find membranes that are impermeable to such solutes. Osmotic pressure measurements are used for studying polymers because osmotic changes are larger than the changes in boiling point elevation, freezing point depression and vapour pressure lowering. Another advantage of osmotic pressure method is that the presence of a slight trace of an impurity of low molecular weight may cause serious error in freezing point or boiling point elevation whereas it would pass through the cellophane membrane and, therefore, would not change the pressure measured.

Osmotic pressure ( $\pi$ ) of a solution is defined as the pressure that must be applied to the solution so as to totally prevent the flow of the solvent through the semipermeable membrane into the solution.

There are different types of osmometers. These osmometers are divided into two categories, depending on whether the static or the dynamic equilibrium method has been used to determine the osmotic pressure.

(i) Static equilibrium method

(ii) Dynamic equilibrium method.

#### (i) Static equilibrium method :

**The apparatus :** The apparatus consists of two metallic blocks made of stainless, one face of each block having a series of concentric grooves. These grooves, in turn, are interconnected by vertical-horizontal channels. A semipermeable membrane is placed in between these grooved faces of the two metallic blocks. On bolting the apparatus, the two internal grooved faces of the metallic blocks come in close contact through the semipermeable membrane. The solvent and the solution are kept in the space formed between the grooves on the two blocks and are prevented from freely mixing by the membrane separating them. The vertical channels of the blocks are connected to glass capillaries through a drill in the metallic blocks of the solvent and solution compartments.

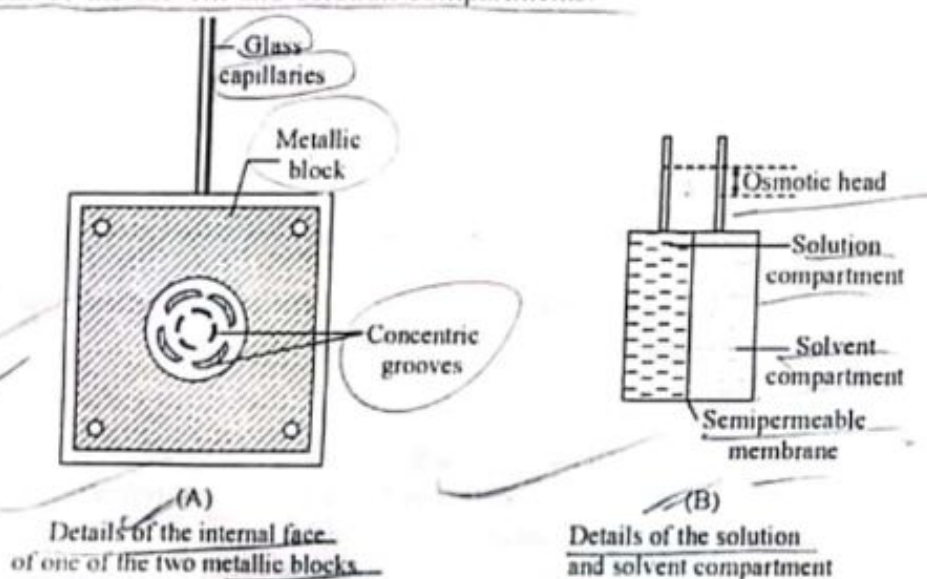


Fig. 2.9. Schematic diagram of static equilibrium osmometer

**Experiment :** First, the two compartments are filled with solvent and the solution of known concentration. Due to the osmotic pressure, the solvent will start passing through the membrane to the



solution side. So the liquid level in the capillary attached to the solution side will rise. This will continue until the hydrostatic pressure developed in the capillary due to the rise of solution level exactly balances the osmotic pressure. Once the osmotic equilibrium is attained, the solvent stops entering the solution side. Then, the height difference between the solution and the solvent levels in the two capillaries is measured. This difference is known as the osmotic head. The same procedure is repeated with solutions of different concentrations and the corresponding osmotic heads are measured.

Theory : The van't Hoff equation relating the osmotic pressure of a polymer solution with the molar mass of the polymer is :

$$\frac{\pi}{C} = RT \left[ \frac{1}{M_n} + B_2C + B_3C^2 + \dots \right] \quad \text{Imp}$$

\* The quantity  $\frac{\pi}{C}$  is called reduced osmotic pressure and  $B_2, B_3$  etc. are the second, third virial coefficients. If the third term is neglected, a graph of  $\pi/RTC$  versus  $C$ , extrapolated to  $C=0$ , gives the intercept on the  $\pi/RTC$  axis as  $\frac{1}{M_n}$ , that is,

$$\left( \frac{\pi}{C} \right) = \frac{RT}{M} \quad \text{or} \quad \left( \frac{\pi}{RTC} \right) = \frac{1}{M_n}$$

*Number average molecular weight can be calculated*

From the intercept, the number-average molecular weight can be calculated.

The demerit of this method is that since the diffusion of solvent through the membrane is a very slow process, the time taken to attain equilibrium is very high.

**(ii) Dynamic Equilibrium Method :**

The high speed membrane osmometer (HSMO) is commonly used now-a-days. It is a rapid method and attains equilibrium within 5 to 7 minutes. There are two parts in this osmometer. The upper part

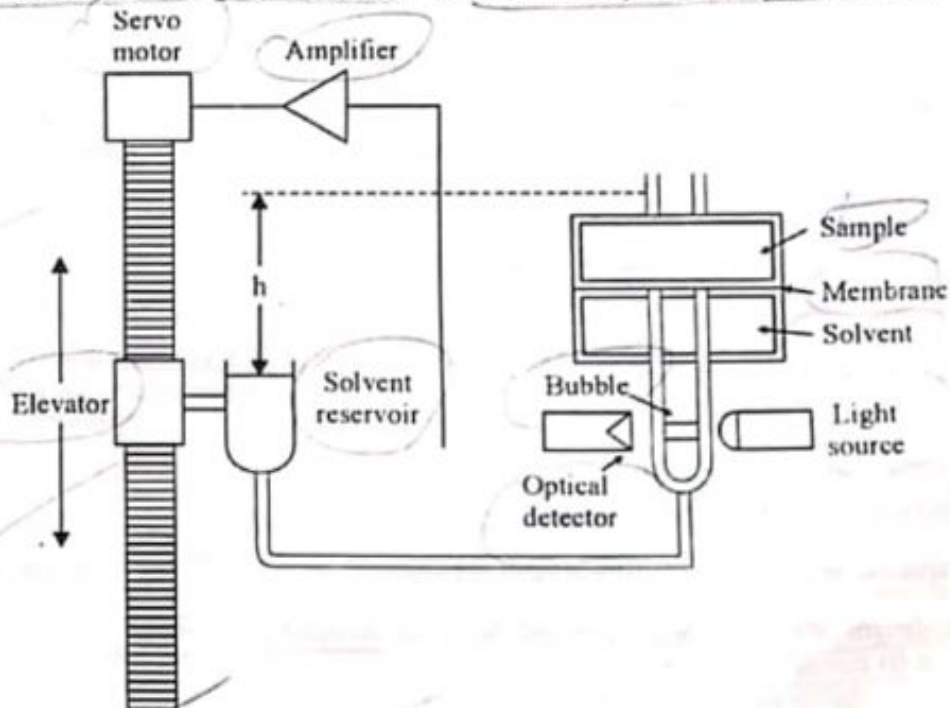


Fig. 2.10. Schematic diagram of essential components of a high speed membrane osmometer