2

THE LIQUID STATE

2.1 INTRODUCTION

The structure of a molecule can be studied by finding out the size and shape of the molecule and the arrangement of its constituent atoms. In this connection, the determination of the lengths of bonds or inter atomic distance and the bond angle is also necessary. To obtain information regarding the configuration and structure of molecule, some typical physical properties, such as surface tension, refractivity, dipole moment, parachor etc., have been employed which are more refined in character, and which measure the property more directly and accurately. These physical properties can be classified into following four group:

(i) additive properties,
(ii) colligative properties,
(iii) constitutive properties,
(iv) additive and constitutive properties.

(i) Additive Properties: Additive properties are those properties which is the sum of the corresponding properties of the atoms constituting the molecule. These properties only depend on the types of the atom and their numbers e.g., mass is a additive property, similarly molar volume is also a good example of additive properties.

(ii) Colligative Properties: Colligative properties are those properties, which depends upon the number of molecules present in a substance e.g., osmotic pressure of the solution, pressure of gas, elevation in boiling point etc.

(iii) Constitutive Properties: Constitutive property of a molecule is the property which depends upon the constitution of the molecule, i.e., upon the arrangements of atoms within the molecule e.g., optical activity.

(iv) Additive and Constitutive Properties: The physical property which depend upon the number of atom in a molecule as well as their constitution, is known as additive and constitutive properties. e.g., atomic volume, parachor etc.

2.2 SURFACE TENSION

The cohesive forces (force between like molecule) between liquid molecules are responsible for the phenomenon known as surface tension. The molecule at the surface do not have other like molecules on all sides of them and consequently they cohere more strongly to those directly associated with them on the surface. This forms a surface ‘film’ which makes it more difficult to move an object through the surface than to moves it when it is completely submersed. Hence, surface tension is a property of liquids arising from unbalanced molecular cohesive forces at or near the surface, as a result of which the surface tends to contract and has properties resembling those of a stretched elastic membranes or surface tension is the energy required to stretch a unit change of a surface area. According to Encyclopedia "surface tension, is the tendency of liquids to reduce their exposed surface to the smallest possible area. A drop of water, for example tends to assume the shape of a sphere. Since the sphere offers the smallest area for a definite volume, the phenomenon is attributed to cohesion. The molecule with in the liquid attacted equally from all sides resulting a net force is zero, but those near the surface experience unequal attraction, because these molecules are pulled inward by the other molecule deeper in side the liquid but there are no liquid molecules on the outside to balance these force and thus they are drawn towards the centre of the liquid mass by this net forces. The surface then appears to act like an extremely thin membrane, and the small volume of water that makes up a drop assume the shape of a sphere, held constant when an equilibrium between the internal pressure and that due to surface tension is reached.

Surface tension is measured in newtons per meter (Nm^{-1}) and is represented by the symbol σ or y or T and its dimensional analysis shown that the unit of surface tension (Nm^{-1}) are equivalent to Joules per square meter (Jm^{-2}). This means that surface tension can also be considered as surface energy. If a surface with surface tension σ is expended by a unit area then the increase in the surface energy is also equal to σ.

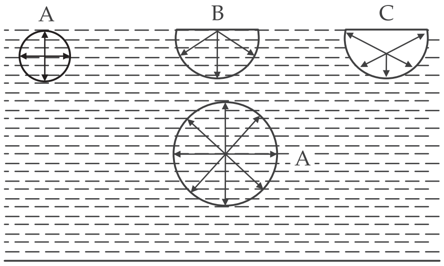


Fig. 2.1 Demonstration of Surface Tension

2.2.1 Examples of Surface Tension

Some important examples of surface tension are given below:

(i) Floating a Needle: If we place a small needle on the surface of water, it can flot on the surface of water even though it is several times as dense as water. If the surface is agitated to break up the surface tension, than needle will quickly sink.

(ii) Walking on Water: Small insects such as the water strider can walk on water because their weight is not enough to penetrate the surface.

(iii) Cleaning of Clothes: Soaps and detergents help the cleaning of clothes by lowering the surface tension of the water so that it more readily soaks into pores and soiled areas.

(iv) Clinical Test for Jaundice: Normal urine has a surface tension of about 66 dynes/cm, but if bile is present (a test for jaundice), it drops to about 55. In the Hay test, powdered sulphur is sprinkled on the urine surface. It will flot on normal urine, but sink if the surface tension is lowered by the bile.

(v) Surface Tension Disinfectants: Disinfectants are usually solution of low surface tension. This allow them to spread out on the cell walls of bacteria and disrupt them. One such disinfectant (S.T. 37), has a name which points to its low surface tension compared to the 72 dynes/cm for water.

(vi) Don't Touch the Test: Common tent materials are some what rainproof, in that the surface tension of water will bridge the pores in the finely woven material. But, if you touch the tent material with your finger, you break the surface tension and the rain well drop through.

2.2.2 Unity of Surface Tension

The most common unit of surface tension are dynes/cm.

Converting dynes/cm to other surface tension units:

1 dynes/cm = 0.001 N/m = 0.0000685 16 f/ft = 0.571 × 10^{-5} = 16 f/n = 0.0022 poundal/ft = 0.00018 poundal/in = 1.0 *n*N/m = 0.001 J/m^2 = 1.0 erg/cm^2 = 0.00010197 kgf/m.

Table 2.1 Surface Tension of Some Common Liquids

Liquid	*Surface Tension (dynes/cm)*
Benzene	28.9
Carbon tetrachloride	27.0
Chloroform	27.1
Diethyl ether	72.8
Ethanol	22.8
Ethyl alcohol	22.3
Glycerol	63.4
Mercury	46.5
Water 20°C	72.75
Water 100°C	58.9

2.2.3 Variation of Surface Tension with Temperature

The surface tension of all liquids decrease with increasing temperature and become zero at the critical temperature because at the critical temperature there is no surface of separation between the liquid and the vapours. To represent the variation of surface tension of a liquid with temperature, many equations have been proposed. Some of them are given below:

(i) Eotvos Equation (1886): According to this equation

$$\mathrm{Y}\left(\frac{\mathrm{M}}{d_{\mathrm{l}}}\right)^{2/3} = \mathrm{K}\,(t_c - t) \qquad \ldots(\mathrm{i})$$

where *Y* is the surface tension of the liquid at temperature T and K is a constant independent of temperature. M, d_l and t_c are the molecular weight, density and the critical temperature of the liquid respectively. Since $\left(\frac{\mathrm{M}}{d_l}\right)$ is the molar volume the factor $\left(\frac{\mathrm{M}}{d_l}\right)^{2/3}$ is proportional to the molar surface area of the liquid and the product, $\mathrm{Y}\left(\frac{\mathrm{M}}{d_l}\right)^{2/3}$ gives the molar surface energy. From equation (i), it is clear that molar surface energy varies with temperature in a linear manner and becomes zero at the critical temperature.

(ii) Ramsay-Shields Equation (1893): The equation proposed by W. Ramsay and J. Shields, is a modification over the Eotvos equation and is expressed as

$$\mathrm{Y}\left(\frac{\mathrm{M}}{d_l}\right)^{2/3} = \mathrm{K}\,(t_c - t - 6) \qquad \ldots(\mathrm{ii})$$

This equation holds good for many liquids. According to this equation *Y* will be zero at a temperature 6° below the critical point and will become negative at the critical point.

(iii) Katayama's Equation: Katayama's replaced ($t_c - 6$) by t_c in the Ramsay-Shields equation to obviate the difficulty that Y is zero at $t = t_c - 6$ and proposed the following equation:

$$\mathrm{Y}\left(\frac{\mathrm{M}}{d_l - d_v}\right)^{2/3} = \mathrm{K}\,(t_c - t) \qquad \ldots\text{(iii)}$$

where, d_v is the density of vapour above the liquid at temperature t.

(iv) Macleod's Equation (1923): The equation is

$$\mathrm{Y} = \mathrm{C}\,(d_l - d_\mathrm{v})^4 \qquad \ldots\text{(iv)}$$

where, d_l is the density of the liquid and d_v is the density of the vapour, both measured at the same temperature.

C is a constant, characteristic of each liquid but is independent of temperature.

This equation holds good with accuracy over a large temperature range for liquids which do not associate or dissociates.

In equation (i), (ii) and (iii), the value of the constant K, was found to be 2.12 for all liquids that behave normally. However, those liquids such as water, alcohol, carboxylic acids etc., which are associated, gives not only abnormally low values of K but also showed variation of K with temperature. For some liquids which dissociate, the value of K was found to be higher than 2.12.

2.2.4 Interfacial Tension

The surface tension measured against another immiscible or partially miscible liquid is referred to as interfacial tension. Consider two immiscible liquid A and B in contact with each other. If γ_A and γ_B are their respective surface tensions, then the interfacial tension γ_AB exists at the boundary between the two layers. Interfacial tension can be measured by the same methods that are employed for determining the surface tension of the pure liquids. For instance, in the drop weight method. The drops of the liquid may be counted in the liquid against which the interfacial tension is to be measured. The interfacial tension value γ_AB is generally intermediate between the surface tensions of two liquids, γ_A and γ_B. It is given by $\gamma_\mathrm{AB} = \gamma_\mathrm{A} - \gamma_\mathrm{B}$. Sometimes interfacial tension may be lower than the surface tension of the either liquid. For example, at 20°C, the surface tension of water and carbon tetrachloride are 72.75 and 26.8 respectively. Their interfacial tension is equal to 45.0, which is very nearly equal to the difference of their surface tension. But in the case of water and ethyl either, the interfacial tension at 20°C is 10.7 which is lower than the surface tension of water and ethyl ether at the same temperature (surface tension of water and ethyl ether at 20°C are 72.75 and 17.0 respectively). The phenomenon of interfacial tension is of considerable importance in connection with the properties of emulsions, detergents, foams etc.

Example 1. *From the following data:*

t°C	d_l *gm/cm*^{3}	γ *dynes/cm*
0°C	0.927	4.5
20°C	0.772	1.16

Calculate t_c *for carbon dioxide using Ramsay equation.*

Solution. According to Ramsay equation

$$\gamma\left(\frac{\mathrm{M}}{d_l}\right)^{2/3} = \mathrm{K}\,(t_c - t - 6)$$

$$\mathrm{M} = 44$$

Substituting the various values for the data at 0°C (273.16 K)

$$4.5\left(\frac{44}{0.927}\right)^{2/3} = \text{K}\,[t_c - (273.16 + 6)]$$

$$140.85 = \text{K}\,(t_c - 279.16)$$

or similarly, substituting the various values at 20°C (293.16 K)

$$1.16\left(\frac{44}{0.772}\right)^{2/3} = \text{K}\left[t - c\,(293.16 + 6)\right]$$

$$36.31 = \text{K}\left[t_c - (299.16)\right]$$

or taking the ratio of the two equations

$$\frac{140.85}{36.31} = \frac{(t_c - 279.16)}{(t_c - 299.16)}$$

$$t_c = 306.1\ \text{K}$$

$$= 33°\text{C}$$

2.2.5 Measurement of Surface Tension

For the measurement of surface tension following method are used:

(i) The Capillary Rise Method: Capillary rise method is the most accurate method for determining the surface tension. It is based on the fact that any liquid (such as water) which wets the walls of a glass capillary tube, will rise in the tube when the tube is placed in the liquid, on the other hand, if a liquid (such as mercury) which does not wet the walls of the capillary tube will not rise and show a depression in the level of the capillary tube is based on the surface tension.

Suppose a fine capillary tube of uniform radius *r* placed in a liquid (that wets the walls of the tube) of density *d*. Now due to force of surface tension γ (which acts along the inner circumference of the liquid) liquid will rise through a height *h*. (The liquid keeps on rising until upward force F_1 due to surface tension is balanced by the downward force F_2, due to the weight of the liquid) then the force acting in upward direction holding the liquid in the capillary i.e., the total force F_1 due to surface tension raising the liquid column upward

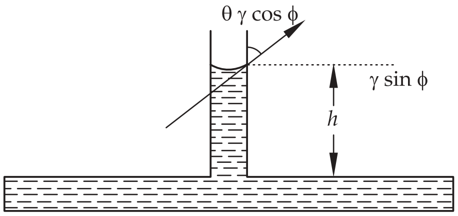


Fig. 2.2 Capillary Rise Method

$$F_1 = 2\pi r\gamma \cos\theta \text{ dynes}$$

where γ = surface tension of liquid

θ = contact angle

Now if the liquid rise a height *h* in the tube above the level of the liquid outside, the downward force, F_2 i.e., force of gravity pulling the liquid downward

$$F_2 = \pi r^2 hdg \text{ dynes} \qquad \ldots\text{(ii)}$$

where, g = gravitational force

At equilibrium, both the forces (F_1 and F_2) will balance each other and hence

$$2\pi r\gamma \cos\theta = \pi r^2 hdg$$

$$\gamma = \frac{rhdg}{2\cos\theta} \qquad \ldots\text{(iii)}$$

If the wetting is perfect, i.e., the angle of contact between glass and liquid is zero, then the equation (iii) reduce to

$$\gamma = \frac{rhdg}{2} \qquad \ldots\text{(iv)}$$

Thus, by measuring the height (h) through which the liquid rise and the radius r of the capillary tube, it is possible to calculated the surface tension of any liquid with the help of equation (iv). The height is measured by a cathetometer and the radius of the capillary tube by a travelling microscope. It should be noted that the weight of the liquid in the meniscus has not been taken into consideration in the above relation. For accurate works, the following two corrections should be made:

(i) correction for the volume of the meniscus,

(ii) correction for the density of the vapours collected above the liquid

Considering these correction, equation (iv) is modified as

$$\gamma = \frac{1}{2}\left(h + \frac{r}{3}\right)(d_l - d_v)\, rg$$

where d_l is the density of the liquid and d_v is the density of the vapour above the liquid.

(ii) Drop Formation Method: A drop of liquid is allowed to form at the lower end of a capillary tube. The drop is supported by the upward force of surface tention acting at the outer circumference of the tube. The weight of the drop (mg) pulls it downward.

When the two forces are balance, the drop breaks

i.e. $mg = 2\pi r\gamma$

Then the surface tension is determined by one of the two method given below:

(a) The Drop Weight Method

(b) Drop Number Method

(a) The Drop Weight Method: It is quite convenient and reasonable accurate method and mainly use to compare the surface tension of the two liquids. The method is based on the fact that when the liquid, whose surface tension is to be determined, is allowed to pass drop by drop through a capillary tube held vertically, every drop coming out of the capillary tube, grows spherically in size and attains some definite weight. When the weight of the drop becomes equal to the force of surface tension, acting along the circumference of the capillary tube, it falls. The relationship between the weight of the falling drop (W) and surface tension (γ) is:

$$\gamma = \frac{Wg}{2\pi rf} \qquad \ldots\text{(i)}$$

where, f is equal to $\frac{r}{v^{1/3}}$, v being the volume of the drop and r its radius.

Practically it is difficult to determine all the factors on the right hand side of above equation (i). Thus, for convenience, surface tension of two liquids flowing separately through the same capillary tube is compared.

If γ^1 and γ^2 are the surface tension of two liquids, the two are related by the equation

$$\frac{\gamma^1}{\gamma^2} = \frac{W_1}{W_2} \qquad \ldots\text{(ii)}$$

where W_1 and W_2 are the weights of drops of lqiuids 1 and 2 respectively.

The instrument used for the purpose is known as the stalagnometer and consists of a bubbled capillary as shown in the figure 2.3. The tube in this instrument is washed thoroughly, dried and is fitted by sucking upto some certain mark *A* with liquid is then allowed to fall very slowly in the form of drops which are collected in a weighing bottle. The number of drops falling per seconds is counted and their weight is determined. If W_1 and W_2 are the mean weight of drops of the two liquids and γ^1 and γ^2 are their surface tensions respectively, they are related to each other by equation (i).

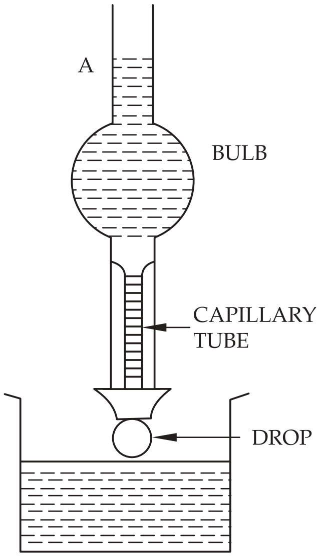


Fig. 2.3 Stalagnometer

It is convenient of determine the number of drops formed by a definite volume of a liquid than to determine the weight of the drop.

Let n_1 and n_2 be the number of drops of equal volume (say V) of two liquids 1 and 2 densities d_1 and d_2 respectively.

The mean weight of drops of liquid 1 and is given by

$$W_1 = \frac{V}{n_1} + d_1 \qquad \ldots\text{(ii)}$$

and the mean weight of liquid 2 is given by

$$W_2 = \frac{V}{n_2} + d_2 \qquad \ldots\text{(iv)}$$

(weight of drop = volume of drop × density)

By putting the values of W_1 and W_2 in equation (ii), we get

$$\frac{\gamma^1}{\gamma^2} = \frac{\frac{V}{n_1} \times d_1}{\frac{V}{n_2} \times d_2}$$

$$\frac{\gamma^1}{\gamma^2} = \frac{d_1 n_2}{d_2 n_2} \qquad \ldots\text{(v)}$$

In this way by knowing the densities and the number of drops formed by the equal volume of the two liquids, the surface tension is calculated by using the equation (v).

(b) Drop-Number Method: In this method the drop pipette is filled upto the mark “A” with the experimental liquid (No. 1). The number of drop is counted as the meniscus travels from A to B. Similarly, the pipette is filled with the reference liquid (No. 2), as the meniscus passes from A to B. Let n_1 and n_2 be the number of drop produced by the same volume V of the two liquid.

Thus,

The volume of one drop of liquid $1 = \frac{V}{n_1}$

The mass of one drop of liquid $1 = \left(\frac{V}{n_1}\right) d_1$

Where, d_1 is the density of liquid 1.

Similarly,

The mass of one drop of liquid $2 = \left(\frac{V}{n_2}\right) d_2$

Then,

$$\frac{\gamma_1}{\gamma_2} = \frac{\left(\frac{V}{n_1}\right) d_1}{\left(\frac{V}{n_2}\right) d_2} = \frac{n_2 d_1}{n_1 d_2}$$

The value of d_1 is determined with a Pyknometer knowing d_2 and γ_2 from reference tables, γ_1 can be calculated.

Example: *In the determination of surface tension of a liquid by the drop number method, it gives 55 drop, while water gave 25 drop for the same volume. The densities of the liquid and water are0.996 and 0.800 g/cm^3 respectively. Find the surface tension of the liquid if that of water is 72.0 dynes/cm.*

Solution. We know that $\frac{\gamma_1}{\gamma_2} = \frac{n_2 d_1}{n_1 d_2}$

where,

$$\gamma_2 = 72.0,\ n_1 = 55,\ d_1 = 0.996 \text{ and } d_2 = 0.800$$

$$\gamma_1 = \gamma_2 \times \frac{n_2 d_1}{n_1 d_2}$$

$$\gamma_1 = 72 \times \frac{0.996 \times 25}{0.800 \times 55}$$

$$= 40.7$$

Therefore, the surface tension of the given liquid is 40.7 dynes/cm.

(iii) The Ring Method or Tensiometric or Torsion Balance Method: This method is used for rapid determination of surface tension in industrial laboratories specially when the quantities of the liquid available are very small. This method involves the measurement of the force necessary to detach a platinum ring from the surface of the liquid with the help of torsion or tensiometer apparatus, which was devised by du Nouy of the Rockfeller institute of medical research.

In this method, a platinum ring about 4 cm in circumference is immersed in the liquid to be tested from the end of the beam of a torsion balance. The wire to which beam is attached is then subjected to torsion by the working screw S_2 and at the same time the adjustable stand is lowered so that the beam remains horizontal at all times. This is allowed to continue till the ring just comes out of the surface of the liquid. The force required to lift the ring up from the surface of the liquid is measured by the angle through which the pointer S, attached to the screw S_2 has to be moved on the graduated disc. Suppose the torsion angles of two liquids are θ_1 and θ_2, then the angle of torsion will be proportional to the downward pull on the ring due to the surface tension of the liquid acting on it. Thus,

$$\frac{\gamma_1}{\gamma_2} = \frac{\theta_1}{\theta_2}$$

where, γ_1 and γ_2 are the surface tension of the two liquids. If the surface tension of one liquid is known that of other can easily be calculated.

In this method, water should not be used as a standard liquid, because organic vapours which are usually present in the industrial laboratories form an interface at the surface of water, thereby replacing water air interface by water organic vapour interface which has much lower surface tension.

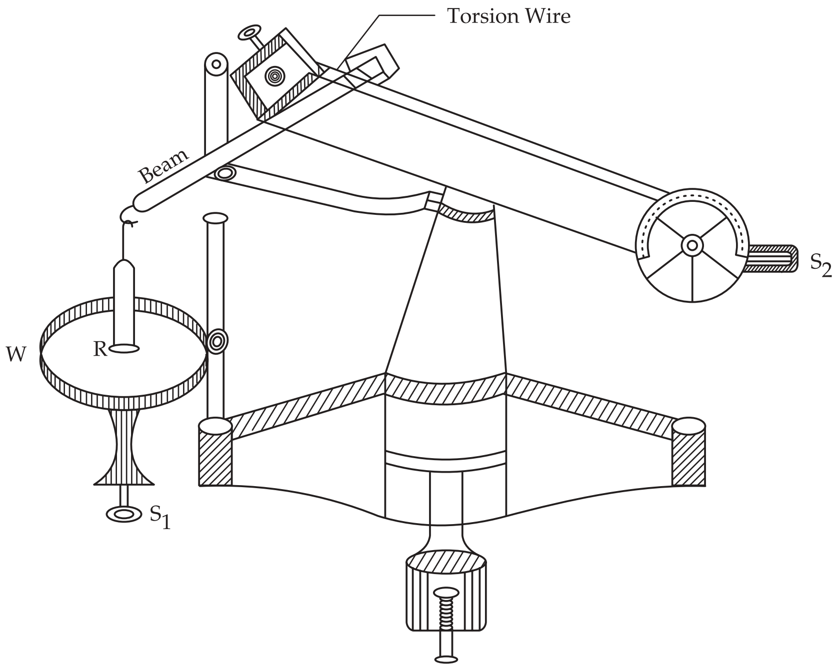


Fig. 2.4 Torsion Balance Method

2.3 VISCOSITY

Viscosity is an internal property of a fluid that offers resistance to flow. It is a measure of the ease with which molecules move past one another. Informally, viscosity is the quantity that describe a fluid resistance to flow. Fluid resist the relative motion of immersed objects through them as well as to the motion of layers with differing velocities within them. Formally, viscosity is the ratio of the shearing stress (F/A) to the velocity gradient in a fluid.

Mathematically, viscosity can be expressed as

$$\mu = \frac{\tau}{\gamma}$$

where, τ = shear stress

γ = shear rate

μ = viscosity

The viscosity of a fluid is a very important property in the analysis of liquid behaviour and fluid motion near a solid boundary.

2.3.1 Common Used Units for Viscosity

The S.I. unit of viscosity is the pascal second [P*a*.S], which has no special name. It is rarely used in scientific and technical publication today. The most common S.I. unit of viscosity is the dyne second per square centimeter [dynes s/cm^2], which is given the name poise [P] after the French physiologist *Jean Louis Poiseuille* (1799-1869).

1 pascal second = 10 poise = 1,000 milli pascal second
1 milli pascal second = 1 centipoise
Centipoise (*c*P) = centistokes (cSt) × density
SSU^1 = centistokes (cSt) 4.55
Degree Engler^1 7.45 = centistokes (*cSt*)
Second Redwood^1 – 4.05 = centistokes (*cSt*)
1 where centistokes are greater than 50.

2.3.2 Types of Viscosity

2.3.3 Dynamic (Absolute) Viscosity

It is the tangential force per unit area required to move one horizontal plane w.r.t the other at unit velocity when maintained a unit distance apart by the fluid. The shearing stress between the layers of non-turbulent fluid moving in straight parallel lines can be defined for a Newtonian fluid as

$$\tau = \mu \frac{dc}{d\gamma} \qquad \ldots(i)$$

where, τ = shear stress

μ = viscosity

Equation (i) is known as the Newtons law of friction.

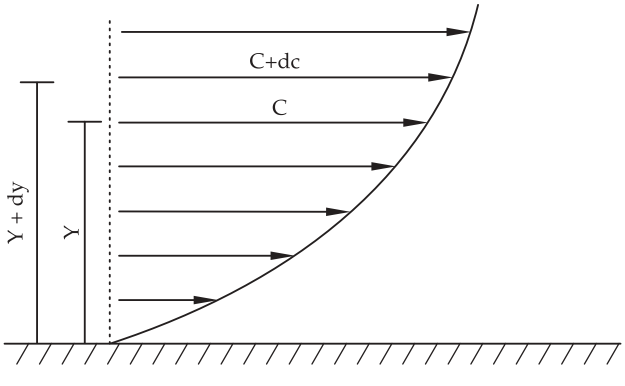


Fig. 2.5 Dynamic Viscosity

In the S.I. system the dynamic viscosity units are Ns/m^2, P*a*S or *kg/ms*, where 1 PaS = 1 Ns/m^2 = 1 kg/ms

The dynamic viscosity is often expressed in the metric C.G.S. system as g/cm s, dynes s/cm^2 or poise (*p*).

where, $1 \text{ poise} = \dfrac{\text{dynes}}{\text{cm}^2} = \dfrac{\text{g}}{\text{cm s}} = \dfrac{1}{10}\text{P}a\text{S}$

For practical use the poise is to large and its usual divided by 100 into the smallest unit called the centipoise (cP) where

$$1\,P = 100\,cP$$

Water at 68.4°F (20.2°C) has an absolute viscosity of one 1 centipoise.

2.3.4 Relative Viscosity

Einstein (1906) derived a relationship for the case of rigid spherical particles in a dilute solution, which is given by

$$\lim_{\phi \to 0}\left[\frac{(n/n_0)-1}{\phi}\right] = 2.5$$

where, n = viscosity of the solution

n_0 = viscosity of pure solvent

ϕ = volume fraction of the solution occupied by solute particles

The ratio n/n_0 is called the relative viscosity, $[n_{r1}]$ of the solution.

2.3.5 Specific Viscosity

Specific viscosity is the relative increase in the viscosity and is given by

$$n_{sp} = \frac{n - n_0}{n_0} = \frac{n}{n_0} - 1 = n_r - 1$$

2.3.6 Reduced Viscosity

The ratio $\dfrac{n_{sp}}{c}$, i.e., the relative increase in viscosity per unit concentration of the solution, is known as reduced viscosity. It depends upon the molecular weight of the substance such as a polymer. Since reduced viscosity depends upon the concentration, it is necessary to extrapolate a graph of $\dfrac{n_{sp}}{c}$ against c to zero concentration i.e., $c = 0$. This extrapolated value is called intrinsic viscosity and is denoted by $[n]$.

2.3.7 Molecular Viscosity

Although viscosity varies rapidly with the temperature, but the product of it and the molecular surface $(M/d)^{2/3}$ has been found to be independent of temperature and is called molecular viscosity.

Thus, molecular viscosity $= \left(\dfrac{\text{M}}{d}\right)^{2/3} \times n$

According to Thorpe and Rodger (1894), the molecular viscosity is an additive as well as constitutive property and is used in elucidating the structures of the compounds. They also prepared a table of values for various atomic and bond contributions, but the results have not been very satisfactory. Molecular viscosities of some atoms and groups are given in Table 2.2.

Table 2.2 Molecular Viscosity of Some Atoms and Groups

Atom or Group	*Molecular Viscosity*	*Atom or Group*	*Molecular Viscosity*
H	80	S	155
C	– 98	C l	284
O in OH	196	Double bond	113
O in ethers	35	Six membered ring	610
O in > C = O	248		

Dunstan (1909) also discovered an important relationship between molecular volume and viscosity. According to him,

$$\frac{d}{\mathrm{M}} \times n \times 10^6 = 40 \text{ to } 60$$

where, *d*, M and *n* are the density, molecular weight and viscosity of the liquid respectively. This expression is applicable only to normal liquids. For associated liquids the value is considerably greater than 60.

2.3.8 (a) Kinetic Viscosity

It is the ratio of absolute or dynamic viscosity to the density, a quantity in which no force is involved.

$$\nu = \frac{\mu}{\mathrm{p}}$$

where, ν = kinetic viscosity

p = density

For the S.I. system the theoretical unit is m^2/s or common used stoke (S*t*) where S*t* = 10^{-4} m^2/s. Stoke is an unpractical large unit, it is usual divided by 100 to give the unit called centistokes (*c*S*t*).

where, 1 S*t* = 100 *c*S*t*

1 *c*S*t* = 10^{-6} m^2/s

2.3.8 (b) Converting between Kinetic and Absolute Viscosity for Air

Kinetic viscosity of air at 1 bar and 40°C is 16.97 *c*S*t* (16.97 10^{-6} m^2/s).

The density of air may be estimated by the ideal gas law:

$$\text{Density} = \frac{10^5}{287313} = 1.113 \text{ kg/m}^2$$

$$\text{Absolute viscosity} = 1.113 \times 16.97 \times 10^{-6}$$

$$= 1.8810^{-5} \text{ kg/ms (Ns/m}^2\text{) } (p)$$

2.3.9 Newtonian Fluids

The relationship in which viscosity is a constant regardless of shear stress or rate of shear is called Newton's viscosity law. Many common solvents, mineral base oils, synthetic base fluid and fully formulated single-grade oils obey Newton's viscosity law, and are called Newtonian fluids. In other words Newtonian fluids are those for which the shearing stress is linearly related to the rate of shearing strain. Newtonian materials are referred to as true liquids since their viscosity of consistency is not affected by shear such as agitation pumping at a constant temperature.

2.3.10 Non-Newtonian Fluids

Non-newtonian fluids are those for which viscosity is not a constant, but varies based upon the rate of shear or the shear stress at which it is measured. The majority of modern motor oils are multi viscosity grade oils that are formulated with high molecular weight polymers called viscosity modifiers. The viscosity of such oils decrease with an increase in shear rate. These are called *shear thinning* fluids. Examples of other non-newtonian fluids are ceiling paint, quicks and and rubber cement.

Table 2.3 Viscosity of Common Substance

Substance	*Viscosity (PoS)*
Air (at 18°C)	1.9×10^{-5} (0.000019)
Water (at 20°C)	1×10^{-3} (0.001)
Canola oil (at room temperature)	0.1
Motor oil (at room temperature)	1
Corn syrup (at room temperature)	8
Pahoehoe lava	100 to 1,000

Table 2.4 Viscosity values and Specific Gravity of Some Typical Liquids

Centipoise (1) *(cP)*	*Centistokes (cSt)*	*Saybolt Second Universal (SSU)*	*Typical Liquid*	*Specific Gravity*
1	1	31	Water	1.0
3.2	4	40	Milk	–
12.6	15.7	80	No 4 fuel oil	0.82 to 0.95
16.5	20.6	100	Cream	–
34.6	43.2	200	Vegetable oil	0.91 – 0.95
88	110	500	SAE 10 oil	0.88 – 0.94
176	220	1000	Tomoto juice	–
352	440	2000	SAE 30 oil	0.88 – 0.94
820	650	5000	Glycerine	1.26
1561	1735	8000	SAE 50 ml	0.88 – 0.94
1760	2200	10,000	Honey	–
5,000	6,250	28,000	Mayonnaise	–
15,200	19,000	86,000	Sour cream	–
17,640	19,600	90,000	SAE 70 oil	0.88 – 0.94
–	–	–	Ink printers	1.0 – 1.38
–	–	–	Sulphuric acid	1.83

(1) Centipoise = Centistokes × Specific gravity

where, specific gravity is assumed to be 0.8 (except for water)

The exact centipoise can be calculated:

$$\text{Centipoise } (c\text{P}) = \text{Centistokes } (c\text{S}t) \times \text{Density}$$

2.3.11 Factors Affecting Viscosity

The factors which effect the viscosity are given below:

(i) Temperature: Viscosity varies with temperature. Honey and syrups can be made to flow more readily when heated. Engine oil and hydraulic fluids thicken appreciably on cold days and significantly affect the performance of cars and other machinery during the winter month. In general, the viscosity of a simple liquid decreases with increasing temperature (and vice versa). As temperature increases, the average speed of the molecules in a liquid increases and the amount of time they spend 'in contact' with their nearest neighbours decreases. Thus, as temperature increases, the average intermolecular forces decreases. The exact manner in which the two quantities vary is nonlinear and changes abruptly when the liquid changes phase.

(ii) Pressure: Viscosity is normally independent of pressure, but liquids under extreme pressure often experience an increase in viscosity. Since liquids are normally incompressible, an increase in pressure doesn't really bring the molecules significantly closer together.

2.3.12 Determination of Coefficient of Viscosity

There are two methods which are generally employed to determine the coefficient of viscosity of a liquid. These methods are based on either the Poiseuille equation or Stokes equation.

(i) Method Based on Poiseuille Equation: Poiseuille in 1842 gave an equation that gives the relationship between the coefficient of viscosity and rate of flow of a liquid through a long and thin tube. The equation is

$$n = \frac{\pi p r^4 t}{8 L \nu} \qquad \text{...(i)}$$

where, ν is the volume of the liquid issuing in time t through a capillary tube of radius r and length L under a constant driving pressure of P *dynes*/*cm*^{2}.

To measure η of a liquid by this method, it is not necessary to determine all the quantities on the right hand side of equation (i). We measure the viscosity of one liquid relative to some other reference liquid, generally water whose coefficient of viscosity has been determined accurately. The usual procedure is to determine the time of flow of fixed volume of two different liquids through the same capillary tube and then compare the two time flow.

If n_1 and n_2 are the coefficient of viscosities of two different liquids of densities, d_1 and d_2 respectively and t_1 and t_2 are the time of flow of the same volume (say v) of the two liquids, then from Poiseuille's equation

$$n_1 = \frac{\pi P_1 r^4 t_1}{8 L \nu}$$

and $$n_2 = \frac{\pi P_2 r^4 t_2}{8 L \nu}$$

where P_1 and P_2 are the pressures on the liquids 1 and 2 respectively.

Taking the ratio of the two equations

$$\frac{n_1}{n_2} = \frac{t_1 P_1}{t_2 P_2} \qquad \text{...(ii)}$$

But, since pressure $\propto$ density of the liquid

$P_1 \propto d_1$ and $P_2 \propto d_2$

$\therefore$ Equation (ii) becomes

$$\frac{n_1}{n_2} = \frac{t_1 d_1}{t_2 d_2} \qquad \text{...(iii)}$$

From equation (iii), η_1 can be calculated, if η_2, d_1 and d_2 are known and t_1 and t_2 determined. The times t_1 and t_2 are easily measured with the help of an instrument known as viscometer.

Ostwald's viscometer essentially consists of a capillary tube AB connected with a bulb C. The lowerend B of the capillary is joined with a wider U shaped tube having a bulb D as show in figure 2.6. The visometer is first washed with chromic acid then with pure distilled water and finally dried. A known volume of water depending upon the capacity of bulb C is now introduced into the viscometer through the end E. It is then sucked into the bulb C with the help of a rubber tube attached at the end of G, till it reaches above the mark F. The liquid is allowed to flow back and time *t* required by the water to flow between mark F and A is noted. Let it be t_1.

The viscometer is dried and the same volume of the liquid (whose viscosity is to be determined) is introduced into the bulb D and again the same process repeated. Let the time of flow now be t_2. Now we know,

$$\frac{n_1}{n_2} = \frac{d_1 t_1}{d_2 t_2}$$

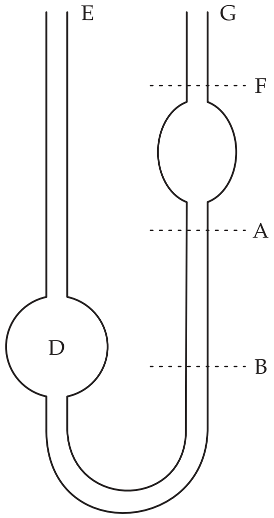


Fig. 2.6 Ost wald's viscometer

where, d_1 and d_2 are the densities of water and liquid respectively.
These can be determined by picknometer or specific gravity method. If the coefficient of viscosity of water at the temperature of the experiment is known, than the coefficient of a liquid can be easily calculated by using equation (iii). The viscosities of some common liquids are given in the following table.

Table 2.5 Coefficient of Viscosities in Millipoise

Liquid	10°	20°	30°	40°
Water	13.097	10.087	8.004	6.536
Toluene	6.71	5.90	5.25	4.71
Chloroform	6.25	5.63	5.10	4.64
Benzene	7.57	6.47	5.61	4.92
Ethyl alcohol	14.66	12.00	10.03	8.34
Methyl alcohol	6.90	5.93	5.15	4.49
Aniline	64.5	42.7	31.1	23.6

(ii) Method Based on Stoke's Equation: Stoke's law deals with the fall of a solid body through a liquid. When a spherical body of radius *r* and density d_s falls under gravity through a liquid of density d_l, it is acted on by the gravitational force, f_1 given by

$$f_1 = \text{Weight of spherical body} - \text{Weight of liquid displaced}$$

$$= \frac{4}{3}\pi r^3 \times d_s \times g - \frac{4}{3}\pi^3 \times d_l \times g$$

$$= \frac{4}{3}\pi r^3 \,(d_s - d_l)\, g \qquad \ldots\text{(i)}$$

The body falling under the gravitational force is opposed by the frictional forces within the liquid. Hence, it does not fall with a continued increase of velocity. The body acquire a constant velocity, called the terminal velocity when the gravitational force,f_1 with which the body falls is just balanced by the frictional force f_2 acting upward f_2 is given by

$$f_2 = 6\pi r n \nu \qquad \ldots\text{(ii)}$$

where, ν is the terminal velocity and n the coefficient of viscosity.

At equilibrium $f_1 = f_2$

From equations (i) and (ii),

$$\frac{4}{3}\pi r^3 (d_s - d_l)\, g = 6\pi r n \nu$$

or $$n = \frac{2r^2 (d_s - d_l)\, g}{9\nu} \qquad \ldots\text{(iii)}$$

Equation (iii) is known as the *Stoke's equation* and is the basis of the falling sphere viscometer which is shown in Fig. 2.7. The liquid whose coefficient of viscosity is to be determined is filled in the viscometer tube *V*.

A small steel ball is then passed through the neck of the tube and the time taken by it to fall between the marks *a* and *b* is measured with a stop watch. If *l* is the distance between the marks *a* and *b* and *t* is the time of fall between these two marks, V is given by

$$V = \frac{l}{t}$$

and equation (iii) becomes

$$= \frac{2r^2 (d_s - d_l)\, g}{9\,\frac{l}{t}} \qquad \ldots\text{(iv)}$$

If the experiment is repeated with the same sphere and another liquid of known density and viscosity, then from equation (iv), the ratio of the two viscosities is given by

$$\frac{n_1}{n_2} = \frac{t_1 (d_s - d_{l_1})}{t_2 (d_s - d_{l_2})} \qquad \ldots\text{(v)}$$

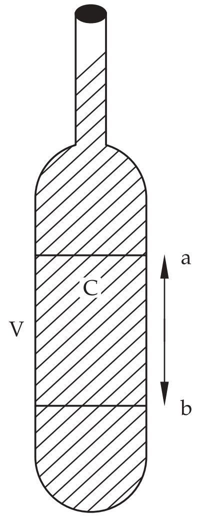


Fig. 2.7 Falling Sphere Viscometer

where d_1 and d_2 are the densities of the two liquids.

Thus, knowing viscosity of one liquid and the times of fall of the same ball through two different liquids of known densities, the relative viscosity of the other liquid under study is easily calculated.

Fluidity (ϕ): This is the reciprocal of viscosity, i.e.,

$$\phi = \frac{1}{n}$$

Fluidity is a measure of the ease with which the liquid flows.

2.3.13 Viscosity and Chemical Constitution

Viscosity is largely due to inter-molecular force of attraction, which resist the flow of a liquid. Therefore, some sort of relationship between viscosity and molecular structures is to be expected. Viscosity is also dependent on the shap, size and mass of the liquid molecules. The following general rules have been discovered.

(i) Dustan Rule: Dustan (1909) showed that viscosity coefficient (n) and molecular volume (d/M) were related as

$$\frac{d}{\mathrm{M}} \times n \times 10^6 = 40 \text{ to } 60$$

This expression holds only for normal (unassociated) liquid. For associated liquid this number is much higher than 60. e.g. The number for benzene (C_6H_6) is 73, while for ethanol (C_2H_5OH) it is 189. This shows that benzene is a normal liquid, while ethanol is an associated one. Thus Dunstan rule can be employed to know wheather a given liquid is normal or associated.

(ii) Molar Viscosity: Please see earlier.

(iii) Rheochor: Newton Friend (1943) showed that if molecular volume (M/*d*) be multiplied by the eight root of coefficient of viscosity, it gives a constant volume [R]. This quantity [R] is known as *Rheochor*

$$[\mathrm{R}] = \frac{\mathrm{M}}{d} \times n^{1/8}$$

The Rheochor may be defined as the molar volume of the liquid at the temperature at which the viscosity is unity. It is a additive as well as constitutive property.

2.4 PARACHOR (SURFACE TENSION AND CHEMICAL CONSTITUTION)

D.B. Macleod in 1923 discovered an interesting relationship between the surface tension and density of liquid. This relationship is known as Macleod equation.

$$\frac{\gamma^{1/4}}{\mathrm{D} - d} = \mathrm{C} \qquad \ldots(\mathrm{i})$$

where, γ = surface tension of the liquid

D = density of the liquid

d = density of the vapour at the same temperature

C = a constant, independent of temperature

The relate surface tension with the chemical constitution of the liquid Sugden in 1924 multiplying both sides of the equation (i) by molecular weight of the liquid (M).

$$\frac{\mathrm{M}\gamma^{1/4}}{\mathrm{D} - d} = \mathrm{MC} = \mathrm{P}\ (\text{constant}) \qquad \ldots(\mathrm{ii})$$

The constant P was known as *parachor.*

At ordinary temperature (for away from the critical temperature) *d* is neglible as compared to D. So the equation (ii) may be written as

$$\mathrm{P} = \frac{\mathrm{M}\gamma^{1/4}}{\mathrm{D}} \qquad \ldots(\mathrm{iii})$$

We know that $\frac{\mathrm{M}}{\mathrm{D}} = \mathrm{V}$, the molar volume of the liquid. So equation (iii) becomes

$$\mathrm{V}\gamma^{1/4} = [\mathrm{P}]$$

If $\gamma = 1$ …(iv)

then $[P] = V$ …(v)

Hence, "parachor of a liquid is the molar volume of the liquid at a temperature at which surface tension of the liquid is unity." It is an additive as well as a constitutive property. If there are two liquid of molecular weight M_1 and M_2 and densitites D_1 and D_2 and surface tension γ_1 and γ_2, then their parachor will be given by

$$P_1 = V_1 \gamma_1^{1/4} \quad \text{…(vi)}$$

$$P_2 = V_2 \gamma_2^{1/4} \quad \text{…(vii)}$$

where, V_1 and V_2 are the molar volumes of two liquids.

By dividing equation (vi) by equation (vii)

$$\frac{P_1}{P_2} = \frac{V_1 \gamma_1^{1/4}}{V_2 \gamma_2^{1/4}} \quad \text{…(viii)}$$

If $\gamma_1 = \gamma_2$ then $\gamma_1^{1/4} = \gamma_2^{1/4}$

Hence $$\frac{P_1}{P_2} = \frac{V_1}{V_2} \quad \text{…(ix)}$$

From the equation (ix) it is proved that (at a definite temperature) if the surface tension of two liquids is equal then the parachor ratio of these two liquids is also equal to their molecular volume. Hence, the parachor may be define as, "it is the measure of molecular volumes on these temperature, when the surface tension of different liquids is same.

Table 2.6 Parachor of Some Esters

S. No.	*Esters*	*Parachor*
(i)	Methyl valerate	292.6
(ii)	Ethyl isobutyrate	292.2
(iii)	Ethyl butyrate	293.6
(iv)	Iso amyl formate	293.6
(v)	Iso butyl acetate	295.1
(vi)	*n*-propyl propionate	295.3

Although parachor is a additive property, but partially it is structural. It have a definite value for every atom and different structure, such as double bond, triple bond, and rings. In 1928 Muford and Philips and then in 1948, Fogel redecide the value of parachor given by Sugden.

Table 2.7 Atomic and Structural Parachor Value

Atom, Group or Bond	*Value of Parachor*		
	By Sugden (1924)	*By Mufard and Philips (1929)*	*By Fogel (1948)*
C (Carbon)	4.8	9.2	8.6
H (Hydrogen)	17.1	15.4	15.7
N (Nitrogen)	12.5	17.5	–
O (Oxygen)	20.0	20.0	19.8
S (Sulphur)	48.2	–	–
F (Fluorine)	25.7	–	–
Cl (Chlorine)	54.3	55.5	55.2
Br (Bromine)	68.0	69.0	68.8
I (Iodine)	91.0	90.0	90.3
P (Phosphorus)	37.7	–	–
C = C, double	23.2	19.0	19.9
$C \equiv C$, triple	46.6	38.0	40.0
– OH group	–	–	30.2
> C = O group	–	–	44.4
– COOH group	–	–	73.7
– NO_2 group	–	–	73.8
3 membered cycle	17.0	12.5	12.3
4 membered cycle	11.6	6.0	10.3
5 membered cycle	8.5	3.0	3.6
6 membered cycle	6.1	0.8	1.4
O (Oxygen) in ester	60.0	–	–
one electron bond	– 11.6	–	–

2.4.1 Atomic Parachors

The contribution of – CH_2 group to the parachor value is about 39. Now it is evident from the table 4 that the parachor value of CH_{10} H_{22}, i.e., decane is 424.2.

Thus, $C_{10}H_{22} = 10\,(CH_2) + 2H$

$$424.2 = 10 \times 39 + 2 \times \text{Atomic parachor of hydrogen}$$

Atomic parachor of hydrogen

$$= \frac{424.2 - 390}{2} = 17.1$$

Similarly, atomic parachor of carbon

$$= CH_2 - 2H$$

$$= 39 - 34.2$$

$$= 4.8$$

From the knowledge of atomic parachors of carbon and hydrogen, it is possible to calculate the atomic parachors of other elements.

2.4.2 Structural Parachors

A comparison of the parachor values from atomic parachor equivalents with those experimentally observed showed a divergence in the case of unsaturated and ring compounds. From this divergence it is clear that parachor are not a additive but also constitutive e.g., parachor value of C_2H_4 was experimentally found to be 99.5 while it should be $2 \times 4.8 + 4 \times 17.1 = 78.0$. The difference between these two value is 21.5. Thus, in this, the double bond and should make a contribution of 21.5. From a careful study of different olefinic compounds, the contribution of a double bond towards parachor has been calculated as 23.2. Similarly a triple bond is shown to make a contribution of 46.6, while the contribution of a single bond has been taken as zero. So with the help of structural parachor we can find out the correct molecule structure of different compounds.

2.4.3 Application of Parachor

There are two important application of parachor:

(i) In Determining the Structure of Molecule: Parachor helps alot in determining the structure or constitution of the molecules.

(a) Structure of Benzene: Molecular formula of benzene is C_6H_6 for which several structure are proposed, but the calculated parachor value is in support of Kekules structure.

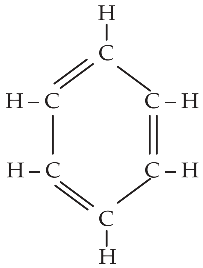
$$[\text{P}] \text{ of } 6 \text{ C atom} = 6 \times 4.8 = 28.8$$

$$[\text{P}] \text{ of } 6 \text{ H atom} = 6 \times 17.1 = 102.6$$

$$[\text{P}] \text{ of } 3 \text{ double bond} = 3 \times 23.2 = 69.6$$

$$[\text{P}] \text{ of one 6 membered ring} = 1 \times 6.1 = 6.1$$

$$\text{Sum of calculated parachor} = 207.1$$



Kekule structure of Benzene

Now the experimental value of parachor for benzene can be obtain as

$$P = \frac{M\gamma^{1/4}}{D}$$

Molecular weight of benzene

$$M = 78.10$$

Density D at 20°C

$$D = 0.878$$

Surface tension γ at 20°C

$$\gamma = 29.3$$

$$\therefore \qquad \text{Parachor of benzene} = \frac{78.10}{0.878} \times (29.3)^{1/4}$$

$$= 206.5$$

Since the experimental parachor value of benzene agree with the calculated value for Kekule structure. Therefore, Kukules structure of benzene is more statisfactory.

(b) Structure of Quinone ($C_6H_4O_2$): The following two structure are given for quinone.

(i) Structure I (Quinonoid structure)

$$[\text{P}] \text{ of } 6\text{ C} = 6 \times 4.8 = 28.8$$

$$[\text{P}] \text{ of } 4\text{ H} = 4 \times 17.1 = 68.4$$

$$[\text{P}] \text{ of } 2\,[\text{O}] = 2 \times 20 = 40$$

$$[\text{P}] \text{ of } 4 \text{ double bond} = 4 \times 23.2 = 92.8$$

$$\text{Sum of calculated parachor} = 230$$

(ii) Benzenoid Structure II

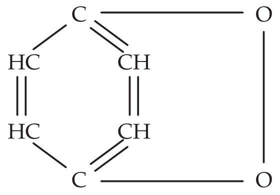
$$[\text{P}] \text{ of } 6\text{ C atom} = 6 \times 4.8 = 28.8$$

$$[\text{P}] \text{ of } 4\text{ H atom} = 4 \times 17.1 = 68.4$$

$$[\text{P}] \text{ of } 2\,[\text{O}] \text{ atom} = 2 \times 20 = 40$$

$$[\text{P}] \text{ of } 3 \text{ double bond} = 3 \times 23.2 = 69.6$$

$$[\text{P}]\ 2 \text{ of } 6 \text{ membered ring} = 2 \times 6.1 = 12.2$$

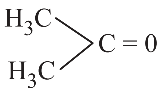


Benzenoid Structure of Quinonoid

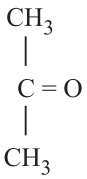
$$\text{Sum of calculated parachor} = 219.0$$

The observed value of parachor (236.8) of quinone is agree with quinonoid structure. Therefore structure I is satisfactory for quinone.

(c) Structure of Acetone: The molecular formula of acetone is C_3H_6O. For it many structure are proposed, out of them one is



Its parachor value can be calculated as



$$\begin{array}{c} CH_3 \\ | \\ C = O \\ | \\ CH_3 \end{array}$$

$[P]$ of 3 carbon atom $= 3 \times 4.8 = 14.4$

$[P]$ of 6 hydrogen atom $= 6 \times 17.1 = 102.6$

$[P]$ of one oxygen atom $= 1 \times 20.0 = 20.0$

$[P]$ of one double bond $= 1 \times 23.2 = 23.2$

Sum of calculated parachor value $= 160.2$

Since the calculatede parachor value of acetone 160.2 is agreed with its experimental value i.e., 161.1. Hence, the above structure for mula is correct for acetone.

(d) Structure of Paraaldehyde: For paraaldehyde following two structure formula are possible.

For structure I

$[P]$ of 6 carbon atom $= 6 \times 4.8 = 28.8$

$[P]$ of 12 hydrogen atom $= 12 \times 17.1 = 205.2$

$[P]$ of 3 oxygen atom $= 3 \times 20 = 60$

$[P]$ of one 6 membered ring $= 1 \times 6.1 = 6.1$

Sum of calculated parachor $= 300.1$

For second structure

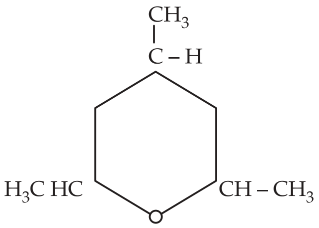
$[P]$ of carbon atom $= 6 \times 4.8 = 28.8$

$[P]$ of 12 hydrogen atom $= 12 \times 17.1 = 205.2$

$[P]$ of 3 oxygen atom $= 3 \times 20 = 60$

$[P]$ of one doubled bond $= 1 \times 23.2 = 23.2$

Sum of calculated parachor $= 317.2$



St. I

$CH_3 \cdot CH(OH) \cdot CH_2CH(OH) \cdot CH_2OH$

St. II

Structure of Paraaldehyde

The experimental value for paraaldehyde is 298.7, which is near with structure I. Hence for paraaldehyde structure I is correct.

(e) Structure of Iso cyanide Group: From the experimental parachor values of methyl, ethyl, phenyl and other isocyanides the parachor value of – NC (iso cyanide group) has been found to be about 65. The two possible structure of – NC group may be denoted as

I		II
$-N=C$	and	$-\overset{+}{N}\underset{\rightarrow}{=}\overset{-}{C}$

Calculated value of parachor	Calculated value of parachor
$= 12.5 + 4.8 + 23.2$	$= 12.5 + 4.8 + 46.6 - 1.6$
$= 40.5$	$= 62.3$

Thus, structure II is prefered which has also confirmed by Raman spectra and dipole moment studies.

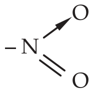
(ii) In Deciding the Nature of Valency Bond

(a) Nitroso Group: Following two structure are possible for nitroso group

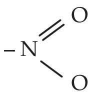
$-\text{N}=\text{O}$	and	$-\text{N}\rightarrow$
Structure I		Structure II

The calculate parachor value for structure I is 55.7 and for structure II it is 30.9, while the experimental value is 55.0 hence for nitroso group its structure I is correct.

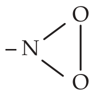
(b) Nitro Group: For this group following structure can be given



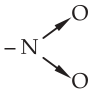
Structure-I



Structure-II



Structure-III

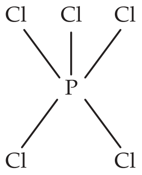


Structure-IV

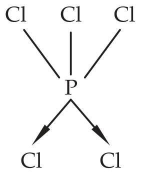
The calculated parachor value for structure I, II, III and IV are 74.1, 98.9, 69.2 and 49.3 respectively. While its experimental parachor value is 73.0. Hence, nitro group is represented by structure I i.e.,

Singlet Linkage: With the help of parachor value Sudgen proved the existence of singlet linkage in many compound.

e.g., The following two structure are proposed for PCl_5



Sidgwick structure
[P] value = 309.2



Sugden structure
[P] value = 286

Sudgen gave the concept of singlet linkage in PCl_5. A chemical bonding developed by only one electron is called a singlet linkage. It is a form of co-ordinate linkage in which a single electron is shared by two atoms. The observed value of parachor for PCl_5 is 284.5, which agrees closely with Sugden structure. Therefore Sugden structure is satisfactory for PCl_5.

PCl_5 on heating decompose to give:

$$PCl_5 \overset{\Delta}{\rightleftharpoons} PCl_3 + Cl_2$$

It clearly shows that three chlorine atom are joined to *P* atom by three covalent bond and remaining two chlorine atom present in the form of singlet linkage. In the same way, the existence of singlet linkage in chelate metallic compounds have also been proposed.

2.5 REFRACTIVE INDEX AND REFRACTIVITY

When a ray of light passes from one medium into another of different density, its direction is changed on passing through the surface.

If the second medium is optically denser than the first, the ray will become more nearly perpendicular to the dividing surface. The angle between the ray in the first medium and the perpendicular to the dividing surface is called the angle in the incidence, i whereas the corresponding angle in the second medium is called the *angle of refraction* r . sin i and sin r are directly proportional to the velocities of the light in the two media. The ratio $\frac{\sin i}{\sin r}$ is called the index of refraction n.

$$n = \frac{\sin i}{\sin r}$$

If the incident ray is in the denser medium, n will be less than one, if in the rarer medium, the value of n will be greater than one. Commonly n is taken as greater than one, the ray passing from the optically rarer medium (usually air) to the denser.

The refractive index of a medium may also be defined as, "the ratio of the velocity of light in vacuum to that in the medium. When a beam of light passes from a rare to denser medium it is easy to show from the law of refraction that

$$\frac{\sin i}{\sin r} = \frac{n_2}{n_1}$$

where, n_1 = refractive index of rarer medium

n_2 = refractive index of denser medium

It is well evident that the angle of incident can never be greater than 90° and when it is 90°, then sin 90° = 1, and the above equation is reduced to the form

$$\sin r = \frac{n_1}{n_2}$$

The refractive index depends upon the temperature and the wavelength of light used. In practice, usually D line of sodium is used for standard measurement.

Refractive index is an easily measurable property of gases, liquid and transparent solids. The index of refraction for two given media varies with the temperature and the wavelength of light and also with the pressure, if we are dealing with gases. If these factors are kept constant, the index of refraction is a characteristic constant for the particular medium and is used in identifying or determining the purity of substance and for determining the composition of homogeneous binary mixtures of known constituents.

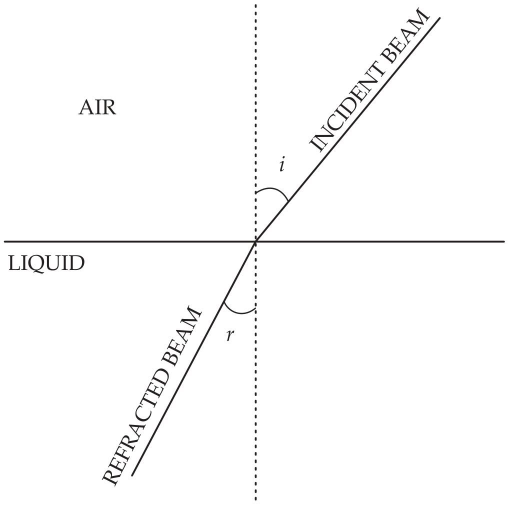


Fig. 2.8

2.5.1 Specific and Molecular Refractivity

The refractive index of a liquid varies with temperature and pressure, but the specific refraction, *rD* is independent of these variables.

$$r\mathrm{D} = \frac{n^2 - 1}{n^2 + 2}\,\frac{1}{\mathrm{P}} \qquad \ldots\text{(i)}$$

where, P = density

n = refractive index

This relationship is given by *Lorentz and Lorentz equation*. The change of refractive index with a change in temperature is compensated by the change in density of the liquid. If the specific refractivity is multiplied by the molecular weight of the substance, the product obtained is called *molecular* or *molar refractivity*.

Thus, molecular refractivity,

$$[\mathrm{R}] = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{\mathrm{M}}{d}$$

where, M is molecular weight of the liquid.

The molecular refractivity of the solid may be determined by dissolving it first in a suitable solvent inorder to get a solution of known concentration. The refractive index and the density of the solution are determiend by usual method.

The molecular refractivity of the solution is then given by the following relationship:

$$[\mathrm{R}] = \frac{n^2 - 1}{n^2 + 2}\left[\frac{n_1 m_1 + n_2 m_2}{d}\right]$$

where, m_1 = molecular weight of the solvent

m_2 = molecular weight of the solute

n_1 = mole fraction of solvent

n_2 = mole fraction of the solute

d = density of the solution

n = refractive index of the solution

The molar refractivity of the solution is also related to molar refractivities R_1 and R_2 of the solvent and solute, respectively, by the following expression:

$$[\mathrm{R}] = n_1 \mathrm{R}_1 + n_2 \mathrm{R}_2$$

From this equation R_2, the molar refractivity of the solid can be calculated, because R_1, the molar refractivity of the solvent is known, or can be determined experimentally.

2.5.2 Factors Affecting Refractive Index Measurement

The most important factors that affect a refractive index measurement are the temperature, pressure and wavelength.

(i) Temperature: The refractive index of a medium is primarily affected by the temperature, because of the accompanying change in density. In the case of many liquids the temperature coefficient of refractive index lies in the range of -4 to -6×10^{-4} degree^{-1}. The coefficient of water is however, -1×10^{-4}, which is an important exception. Similar is the case with aqueous solution. The temperature coefficient of solids are of the order or magnitude smaller than the typical liquids. Evidently, temperature has a marked effect on the refractive index measurement. For the average liquid, temperature fluctuation should be less than $\pm 0.2°C$.

(ii) Pressure: The refractive index of a substance increase with pressure because of the accompanying increase in density. The effects is more pronounced in gases than in liquid. For solids, the effect is smaller than gases and liquids.

Thus, the variation in atmospheric pressure is only important for precise work with gases and for the most exact work with liquids and solids.

(iii) Wavelength: According to the phenomena of normal dispersion, the refractive index of a substance decreases rapidly with increasing wavelength of the radiation. In the vicinity of a absorption bands, however, rapid change in refractive index takes place. The dispersion in this case is known as *anomalous dispersion.*

It is well evident from these dispersion phenomenon, that the wavelength used should be specified in quoting a refractive index. In refractometery, D line from a sodium vapour lamp is commonly used C and F line from a hydrogen source $(\lambda = 6563 \text{ Å})$ and 4861 Å and *G* line of mercury $(\lambda = 4358 \text{ Å})$ are the other lines which have been employed for refractive index measurement.

2.5.3 Measurement of Refractive Index

Two types of instruments for measuring refractive index are available from commerical source.

(i) Refractometers: Refractometers are used for the convenient and rapid determination of refractive index of liquids. Refractometers are based upon the measurement of the so called critical angle (the angle of refraction in a medium when the angle of the incident radiation is 90°).

(ii) Interferometers: These instruments utilize the interference phenomena to obtain differential refractive index with very high precision.

(a) Abbe Refractometer: The Abbe refractometer is used for rapid, though not very accurate measurement. The instrument consists of two glass prims A and B. The hypotonuse surface of a prism B is polished, while that of A is finally ground. The two prisms are enclosed in metal castings hinged at H. The two prism can be rotated about a horizontal axis immediately beneath a telescope T and they can be held in contact with the help of a clamp C. An arm R which is attached with the metal case carrying the prisms, move along a graduated scale, the reading of which gives directly the refractive index of the liquid under examination. The principle and working of *Abbs refractometer* may be illustrated by fig. 2.9.

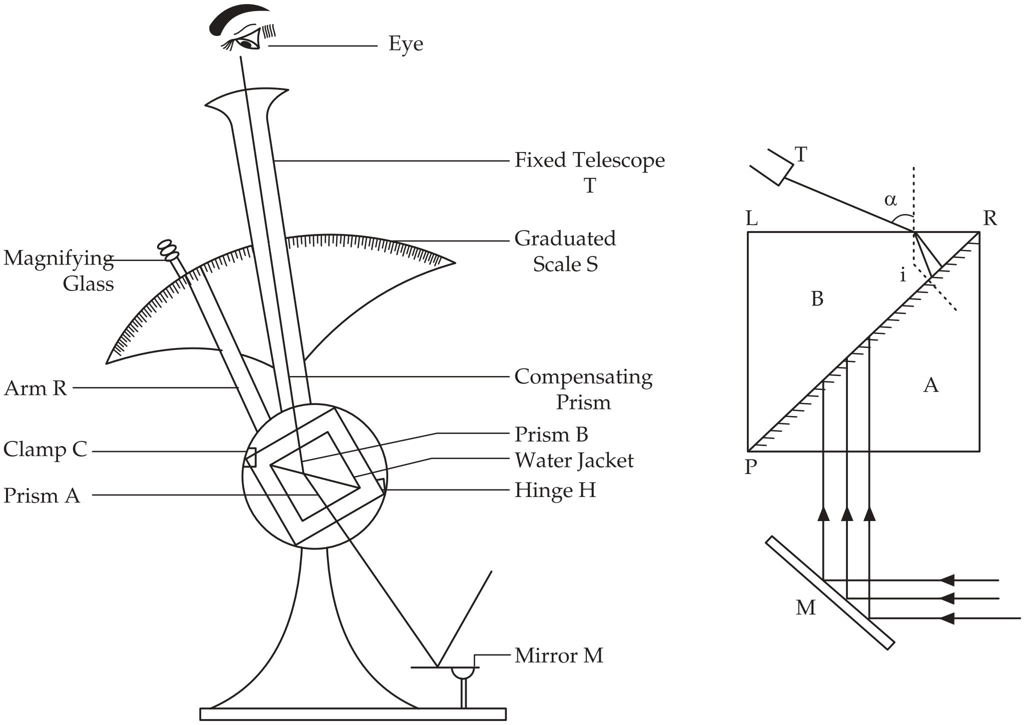


Fig. 2.9 (a) Fig. 2.9 (b)

Fig. 2.9 (a) and (b) Abbs Refractometer

A beam of light from a suitable source is reflected by the mirror M, passes through the lower prism A and illuminates its upper surface PR, A drop of the liquid under examination is placed upon the surface of A. On clamping the prism A and B a film of the liquid spreads between them. As the surface PR is ground, it acts as a diffusion screen providing rays in every direction. It should be noted that the refractive index of the liquid should be smaller than that of the prism A so as to allow for the critical angle phenomena. On reaching the ground surface PR, the light reflected by the mirror M is scattered into the liquid film at different angles of incidence. A particular ray going along the grazing incidence (i.e., at an angle slightly less than 90°) will pass through the prism B at an angle *i* which is equal to the critical angle. In other words, no ray can enter *B* with greater angle of refraction than that of the ray corresponding to grazing incidence. According to critical angle phenomena

$$\sin i = \frac{n}{N}$$

where, *n* and N are the refractive indices of liquid and prism B respectively. The critical ray emerging from the face LR, at an angle α is viewed by means of telescope T. When viewed through the telescope, the field of view is divided into bright and dark portions. The rays entering the liquid at angle less than the grazing incidence will pass through the prism *B* at angle less than the critical angle. Rest of the rays will suffer total internal reflection and will not pass through the prism B. Hence, the band of light viewed through telescope T, finishes sharply at the point where the critical ray, i.e., the edge of the bright portion emerges out of the face LR. In this manner the angle α can be determined vary accurately. Hence the edge of the bright portion when coinside with the cross wire of the telescope gives the refractive index on the scale. When white light is used, a diffused coloured border is seen in the telescope. This may be made sharp and the colours may be removed by the adjustment of two prism (not shown in diagram) attached at the nose of the telescope. In order to maintain temperature constant, the prism A and B are enclosed in a water jecket.

(b) Immersion Refractometer: It is the simplest type of refractometer among all the commercial critical angle instruments. It uses white or artificial light and contains an Amici compensator. As shown in the Fig. 2.10, the prism is immersed in the thermostated sample and white light is reflected from a mirror on to the prism face. After compensation by a single A-mici prism, the refracted radiation is allowed to focus on a linear scale graduated from –5 to + 105 and then observed through the eye piece. The field will be partly dark and partly light, separated by a sharp line. The position of this line is read on the scale, which is equipped with a vernier that permits estimation of boundary position to a small fraction of a scale division. By making use of appropriate tables, it is also possible to convert the readings from the linear scale of the dipping refractometer into refractive indices. The dipping refractometers has widely been used in determining the concentration of aqueous and alcoholic solution. With the help of this refractometer non-albuminous constituents, total globulin, insoluble globulin, albumens and total albumen in even 2 *ml* of serum can be determined with a high degree of accuracy. Inspite of this, it is also used in the identification of unknown substance, in controlling the analysis of commercial products etc. The instrument however, suffers from the disadvantages of limited range, the requirement of large samples, and the resulting greater problems of temperature control.

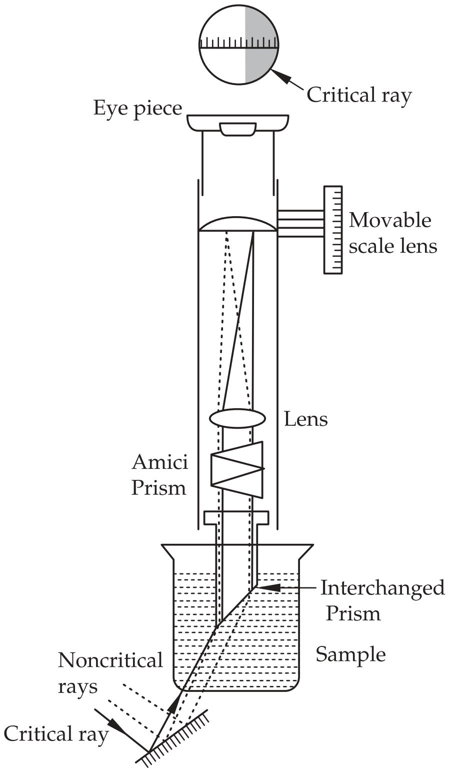


Fig. 2.10 Immersion refractometer

(c) Pulfrich Refractometer: Pulfrich refractometer is used for highly accurate determination. It essentially consists of a small glass cell cemented on the top of a right angled glass prism. The liquid (whose refractive index is to be determined) is placed in the cell and a beam of monochromatic light, such as D line of sodium, is allowed to enter the liquid at grazing incidence along the surface between the liquid and the prism. It should be noted that the refractive index of the prism must be known and it should not be less than of the liquid under examination. The beam of light follows the path ABCD as shown in the figure and is viewed in a telescope. If the telescope is moved in such a manner that it makes an angle less that *i* with the horizontal, no light can be seen. A very accurate determination can, therefore, be made of the angle *i* at which a sharp boundary between a dark and bright field can be seen through the telescope.

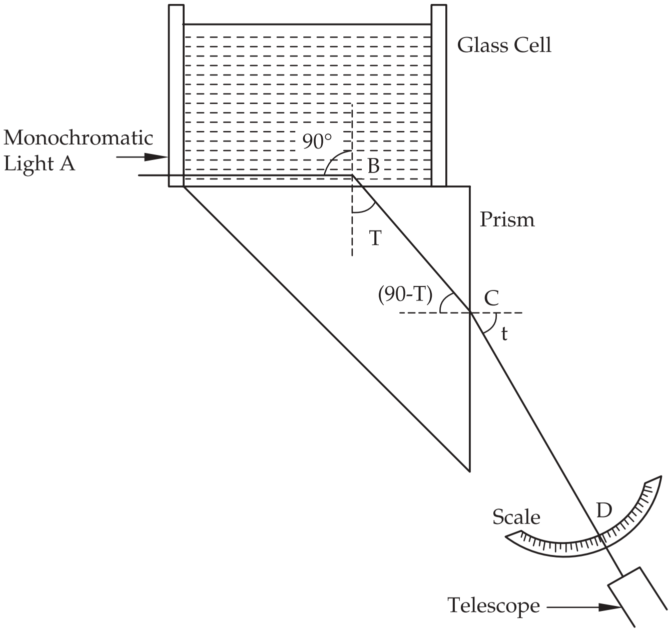


Fig. 2.11 Pulfrich Refractometer

Now suppose *n* and *N* are the refractive indices of the liquid and prism respectively. Then

$$\frac{\sin i}{\sin r} = \frac{N}{n} \qquad \ldots(i)$$

But $i = 90°$, hence $\sin 90° = 1$. Thus

$$\sin r = \frac{n}{N} \qquad \ldots(ii)$$

It is also clear from the above diagram, that

$$\frac{\sin i}{\sin (90° - r)} = N \qquad \ldots(iii)$$

But $\sin (90° - r) = \cos r$, hence

$$\frac{\sin i}{\sin r} = N \qquad \ldots(iv)$$

or $$\cos r = \frac{\sin i}{N}$$

But $$\sin r = \sqrt{(1 - \cos^2 r)}$$

Substituting the values of cos from equation (iv), we have

$$\sin r = \sqrt{\left(\frac{1 - \sin^2 i}{N^2}\right)}$$

But from equation (ii)

$$\sin r = \frac{n}{\mathrm{N}}$$

Thus $$\frac{n}{\mathrm{N}} = \sqrt{\left(1 - \frac{\sin^2 i}{\mathrm{N}^2}\right)}$$

or $$n = \sqrt{(\mathrm{N}^2 - \sin^2 i)}$$

Thus, knowing the refractive index of the prism, i.e. N, and angle of incidence i from the telescope, the refraactive index n of the liquid can easily be calculated. In actual practice, manufactures usually supply a table of $\sqrt{(\mathrm{N}^2 - \sin^2 i)}$ for different values of i which simplies the calculation.

The pulfrich refractometer is some what more accurate than the abbe refractometer. On the other hand, it is less convenient to use particularly in the matter of thermostating of the sample.

2.5.4 Molecular Refractivity and Chemical Constitution

Molecular refractivity is also an additive as well as constitutive property, e.g., in a homologous series of aliphatic compounds, a difference of CH_2 in composition make a difference of 4.62 in molecular refractivity. The contribution of carbon hydrogen atoms have been deduced as under:

The molecular refractivity of $C_7H_{16} = 34.52$

The molecular refractivity of $C_6H_{14} = 29.92$

The molecular refractivity of $CH_2 = 34.52 - 29.92$

$= 4.62$

Thus, the molecular refractivity of H atom $= \dfrac{22.92 - 6 \times 4.62}{2}$

$= 1.10$

and the molecular refractivity of C atoms $= 4.62 - 2 \times 1.10$

$= 2.42$

Knowing the values of atomic refractions of carbon and hydrogen, the atomic and structural refractions of various other element and group have also been calculated.

Table 2.9 Refraction of Atoms and Structures

Atom or Structure	*Refraction*	*Atom or Structure*	*Refraction*
Carbon	2.43	$-C \equiv N$ group	5.46
Hydrogen	1.10	Chlorine	5.97
O in $>$CO	2.21	Bromine	8.86
O in ethers	1.64	Iodine	13.9
O in (OH)	1.53	Doble bond	1.73
N in primary amines	2.32	Triple bond	2.40
N in secondary amines	2.50	Six membered ring	–0.15

With the help of this table, the structure of any compound can be find out e.g.

(i) Structure of Benzene: The Kekule's formula of benzene may be represented as:

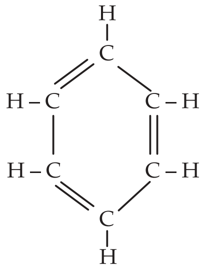


Fig. 2.12 (a) Kekule's structure of Benzene

Calculation of molar refraction

$$6C = 6\times 2.42 = 14.52$$

$$6H = 6\times 1.10 = 6.60$$

$$\text{3 double bond} = 3\times 1.73 = 5.12$$

$$\text{One 6 membered ring} = 1\times(-0.15) = \begin{array}{c} -0.15 \\ \hline 26.16 \end{array}$$

The observed value of molecular refractivity is 26.00. Thus, the calculated value of molecular refractivity is in good agreement with that of observed value. Hence, Kekule formula is correct.

(ii) Structure of Acetylene Dibromide

The structure of acetylene dibromide is:

$$BrCH = CHBr$$

Calculation of molar refraction

$$2C = 2\times 2.43 = 4.86$$

$$2H = 2\times 1.10 = 2.20$$

$$2\,Br = 2\times 8.86 = 17.72$$

$$\text{One double bond} = 1\times 1.73 = \begin{array}{c} 1.73 \\ \hline 26.51 \end{array}$$

The observed value is 26.30. Hence, the formula of acetylene dibromide is varified.

2.6 DIPOLE MOMENT

We know that the covalent bond is formed by the sharing of electron. These covalent bond are of two type, i.e., non-polar and polar.

In non-polar molecule the shared pair of electron lies in the centre of both the atoms at the same distance from both the atom e.g., $Cl - Cl, H_2, N_2$.

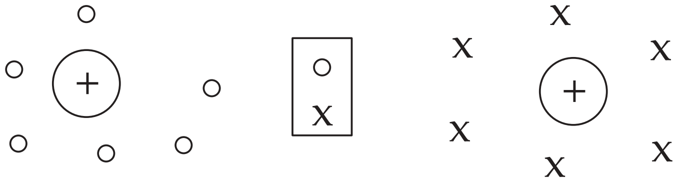
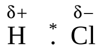


Fig. 2.12 (b) Chlorine Molecule (Non-Polar)

But on the other hand if a covalent bond is formed between two such atoms having different electronegativity. Then such covalent bonded molecule is called polar molecule. In such type of polar molecules the shared pair of electron is slightly shifted towards the atom having more electronegativity in place of lying in the centre, e.g., HCl



$$\overset{\delta+}{H} \overset{*}{:} \overset{\delta-}{Cl}$$

Polar molecule

Due to shifting of shared pair of electron towards more electronegative atom, a negative charge is develop in this atom and a positive charge in the other atom taking part in covalent bond forming.

The multiple of any one quantity of charge and distance between both the charge is known as *dipole moment* and is denoted by μ (mu).

In other words, a polar molecule is one in which there is a separation of the centre of the gravity of the positive and negative charges. The molecule develop a positive and a negative pole. In an electric field the dipolar molecule tend to align themselves in such away that the positive ends faces the positive pole. The polarity of a molecule is quantitatively expressed as its dipole moment. Dipole moment is defined as the product of the charge and the distance of separation of the charge or “the vector equal in magnitude to the product of electric charge (e) and the distance (d) having the direction of line joining positive and negative centres.

$$\mu = e \times d$$

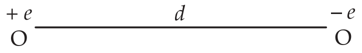


Fig. 2.13 Dipole moment

Since the charge is usually of the order of the charge on the electron i.e., $4.8 \times 10^{-10}\, esu,$ while the distance is of the order of 10^{-8} cm.

$$\mu = 10^{-8} \times 10^{-10} \text{ esu/cm}$$

$$= 10^{-18} \text{ esu/cm}$$

or D (Debye unit) $[\because 10^{-18} \text{ esu/cm} = \text{Debye (D)}]$

$$1\,\text{D} = 10^{-18} \text{ esu/cm} = 10^{-10} \text{ esu A}$$

Hence, a molecule where in the unit positive and negative charges are separated by 0.21 A has a dipole moment of one Dubye.

Dipole moment is a vector quantity as in shown in fig. 2.13.

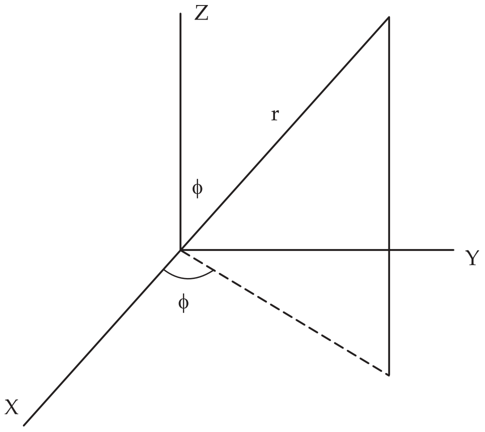


Fig. 2.14 Dipole moment as Vector quantity.

The observed dipole moment of a molecule is the vector sum of the individual dipole moment e.g., CO_2 has a dipole moment zero since the molecule is symmetrical and linear, the vector sum of the bond moments being zero. The dipole moment of water and SO_2 is 1.85 D and 1.60 D respectively, which shows that the molecule is non-linear.

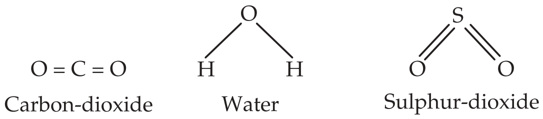


Fig. 2.15 Structure of CO_2, H_2O and SO_2

Table 2.10 Dipole Moment of Some Important Molecules

Molecules	*Dipole Moment*
H_2	0
Cl_2	0
N_2	0
CH_4	0
CCl_4	0
CO_2	0
CO	0.12
HCN	2.93
HCl	1.04
HBr	0.78
HI	0.38
H_2O	1.85
LiH	5.88
H_2S	0.95
NH_3	1.49
SO_3	1.61
NO	0.16
KF	2.55
KCl	2.67
KBR	2.82
H_2O_2	2.20
CH_3Cl	1.87
C_2H_5Cl	2.05
CH_3OH	1.69
C_2H_5OH	1.63
NF_3	0.2

However, electronegativity difference is not the only criterian of polarity. It is also decide by the composition and geometry of the molecule.

From the above table it is clear that NF_3 have smaller dipole moment (0.2 D) as compared to NH_3 (1.46) while the electronegativity difference between nitrogen and fluorine is almost the same as that between nitrogen and hydrogen. The smaller dipole moment of NF_3 is explained on the fact that in case of NH_3 the bond polarity is such that nitrogen is negative and hydrogen are positive, while in case of NF_3 the fluorine are negative but nitrogen is positive. The direction of bond polarity in NF is opposite to that in N – H, but in both cases the contribution of the lone pairs is in the same direction. The smaller dipole moment of NF_3 is thus explained.

Similarly in case of CCl_4 and $CHCl_3$ CCl_4 has four carbon-chloride bond arranged in a symmetric tetrahedral geometry around carbon and therefore despite each C – Cl bond being polar, the centres of gravity of all negative and positive ends coincide on carbon. CCl_4 is thus non-polar. $CHCl_3$ has a different composition and charge distribution and hence the molecule is polar. The arrows in figure point towards the centres of negative charge.

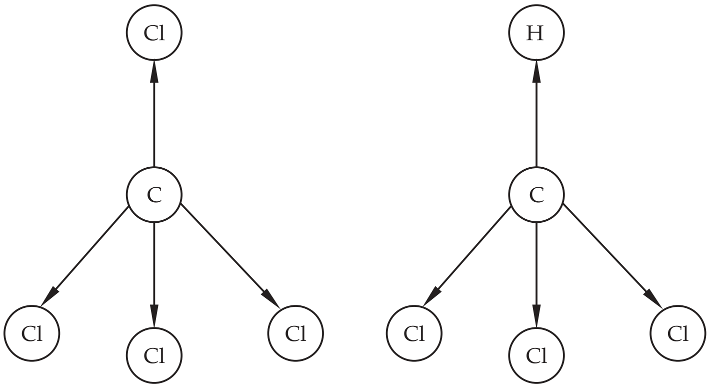


Fig. 2.16 Molecule of CCl_4 and $CHCl_3$

2.6.1 Determination of Dipole Moment

(i) Vapour Temperature or Graphically Method: For molar polarization Debye equation can be written as

$$P_M = \frac{4}{3}\pi N\alpha + \frac{4\pi\mu^2 N}{9K}\left(\frac{1}{T}\right) \qquad \ldots(i)$$

In this equation, the first term of right hand side is a constant, suppose it is A. Similarly in second term (except T) all are constant suppose it is B.

Hence, the equation can be written as

$$P_M = A + \frac{B}{T} \qquad \ldots(ii)$$

While, $A = \frac{4}{3}\pi N\alpha$

and $B = \frac{4}{3} N \frac{\mu^2}{K}$

From equation (ii), it is clear that for polar molecule, if we plot a graph between molar polarization and 1/T, then we obtain a straight line, and the value of whose slove is

$$B = \frac{4\pi N \mu^2}{9K} \qquad \ldots(iii)$$

By putting the value of π, N and K in equation (iii), we get

$$\mu = 0.0128\sqrt{B} \times 10^{-18} \text{ esu}$$

$$= 0.0128\sqrt{B} \text{ Debye unit}$$

In this way, by knowing the value of *B*, we can calculated the dipole moment.

Hence, in the method at first we calculate the value of dielectric constant (ε) and vapour density (P) at different temperature and then by using following equation, the value of molar polarisation can be calculated

$$P_M = \left(\frac{\varepsilon - 1}{\varepsilon + 1}\right)\frac{M}{P}$$

We know that following relationship occured between molar refraction (R_M) and refraction (*n*)

$$R_M = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{M}{P} \qquad \ldots(iii)$$

Hence, $R_M = P_M$

According to Debye equation, molar polarization

$$P_M = \frac{\varepsilon - 1}{\varepsilon + 2} \times \frac{M}{P} \qquad \ldots(iv)$$

$$= P_1 + P_0 \text{ or } P_A + P_B + P_0$$

Since the value of P_A is negligible as compare to P_E. Hence

$$\frac{\varepsilon - 1}{\varepsilon + 2} \times \frac{M}{P} = P_E + P_A \qquad \ldots(v)$$

By putting the value of P_E and P_0 (orientation polarization) in equation (ii)

$$\frac{\varepsilon - 1}{\varepsilon + 2} \times \frac{M}{P} = R_M + \frac{4\pi N \mu^2}{9KT} \qquad \ldots(vi)$$

where, ε = dielectric constant of a substance

P = density of a substance

M = molecular weight of substance

R_M = molar refraction

N = avogadro number

K = Boltzman constant

μ = dipole moment

(ii) Refraction Method: This method is only applicable for non-polar substance (having no permanent dipole moment) Maxwell suggested that for non-polar molecule at high frequency following relation occured between dielectric constant (ε) and refraction (*n*)

$$\varepsilon = n^2$$

At this state (at high frequency) the value of P_0 is zero

$$P_M = P_I = \left(\frac{n^2 - 1}{n^2 + 2}\right) \times \frac{M}{P}$$

where, P_I = induced polarization

P_A = atomic polarization

P_E = electronic polarization

The value of P_A is negeliable as compare to P_E

Hence, $P_I = P_E$

or $$P_E = \left(\frac{n^2 - 1}{n^2 + 2}\right) \times \frac{M}{P}$$

Hence,

For m_1 $$P = A + \frac{B}{T}$$

For m_2 $$P_1 = A + \frac{B}{T_1}$$

$$P - P_1 = B\left(\frac{1}{T} - \frac{1}{T_1}\right)$$

$$B = \frac{P - P_1}{\frac{1}{T_1} \cdot \frac{1}{T_1}}$$

By putting the value of B in following equation, we can calculate the value of dipole moment.

Dipole moment $\mu = 0.0128 \times \sqrt{B}$ Debye

Application of Study of Dipole Moment:

(i) Percentage Ionic Character: With the help of dipole moment we can find out the percentage ionic character of a molecule.

i.e., $$\%\text{ of ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{calculated}}} \times 100$$

Example: *The bond length in HCl molecule is 1.275° A and its observed dipole moment is 1.03. Find out the % ionic character of HCl.*

Solution. Upon ionization of HCl, the charge on hydrogen will be 4.8×10^{-10} esu and on chlorine it is -4.8×10^{-10} esu. Therefore

$$\text{Dipole moment} = q \times r$$

$$= 4.8 \times 10^{-10} \times 1.275 \times 10^{-8} \text{ cm}$$

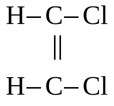
$$= 6.11 \times 10^{-18} = 6.11\,D$$

$$\text{\% of ionic character} = \frac{1.03}{6.11} \times 100 = 16.8\%$$

(ii) Identification of Polar and Non-Polar Molecules: We have seen that molecules with permanent dipoles such as HF, HCl, water etc., are called *polar molecules,* while those without dipoles, such as CCl_4, CO_2 etc. are called *non-polar molecules.*

(iii) Distinction Between Cis and Trans Derivatives in Organic Chemistry: With the help of dipole moment we can distinguishing the cis and trans isomers. The cis form is non-symmetrical, hence the value of its dipole moment is finite, while trans form is symmetrical hence the value of its dipole moment is very less (nearly zero).

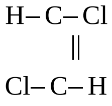
Example: *The value of dipole moment of cis dichloro ethylene is 1.89 D, while the value of trans dichloro ethylene is zero.*



$$\begin{array}{c} H-C-Cl \\ \| \\ H-C-Cl \end{array}$$

cis

$= 1.89$ D



$$\begin{array}{c} H-C-Cl \\ \| \\ Cl-C-H \end{array}$$

trans

$= 0.0$ D

(iv) In the Determination of Bond Angle: With the help of dipole moment, we can also determine the bond angle of a molecule.

Example: The carbon dipole moment of following parabenzyle compound can be calculated with the help of dipole moment.

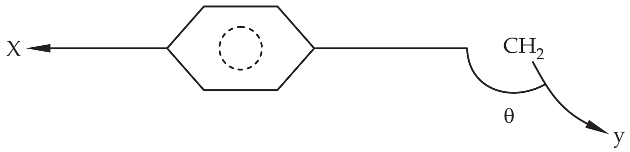


Fig. 2.17 Parabenzyle compound

where, $X = -NO_2, -Cl$ or $-Br$

$Y = -Cl, -Br, -CN$

If the moment of X group is μ_1 and moment of $-CH_2Y$ group is μ_2 and the net moment of this compound is μ, then

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta$$

or

$$\cos\theta = \frac{(\mu^2 - \mu_1{}^2 - \mu_2{}^2)}{2\mu_1\mu_2}$$

Example: *If the dipole moment of O – H bond is 1.53 D and the bond angle between O – H bond is 105°, then calculate the dipole moment of water.*

Solution. We know that

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta$$

$$= (1.53)^2 + (1.53)^2 + 2 \times 1.53 \times 1.53 \cos 105°$$

$$= (1.53)^2 + (1.53)^2 + 2 \times (1.53)^2 \times (-0.2588)$$

$$= (1.53)^2 + [1+1\times(2\times(-0.2588)]$$

$$= 3.4684$$

$$\mu = \sqrt{3.4684}$$

$$= 1.86 \text{ D}$$

(v) Identification of Di substituted Derivated of Benzene: The relative orientation of substituted benzene compound can be determine with the help of dipole moment. Suppose if the angle between the two bonds of di substituted compound is θ, and the moment of both bond is μ_1 and μ_2 respectively, then

$$\mu = \left[\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta\right]^{1/2}$$

The bond angle of di substituted ortho compound is $\theta = 60$, for meta compound bond angle θ is 120° and for para compound angle θ is 180°

μ observed = 6.00 D   3.89 D   0 D

μ calculated = 6.90 D   3.89 D   0 D

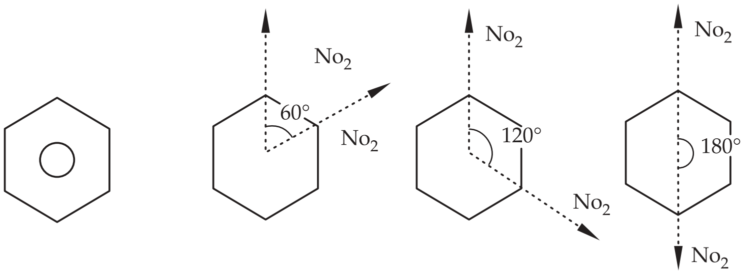


Fig. 2.18 Dipole Moment of Different Dinitro Compound

In the above figure, all the three calculated and observed dipole moment of dinitrobenzene is shown, which shows that as the molecule goes on symmetrical, the dipole moment reduces. The dipole moment of para di nitrobenzene is zero. In ortho dinitrobenzene, the bond angle is less than meta dinitrobenzene, therefore the value of μ is more.

(vi) Resonance Structure: Dipole moment is of great value in determining the contributions of the possible structure in resonating systems. For example, nitrous oxide molecule has a dipole moment which shows that the molecule cannot consist entirely of either of two possible structure.

$$\overset{-}{N} = \overset{+}{N} = O \quad \text{and} \quad N \equiv \overset{+}{N} - \overset{-}{O}$$

Which would have high dipole moment, but that there is resonance between the two forms. Since the molecule of nitrous oxide has a dipole moment, it cannot have a linear structure.

(vii) Geometry and Symmetry of Molecule: Dipole moment has proved to be a powerful and invaluable weapon in our attack of molecular structure. Let us illustrate the usefulness and importance of dipole moment with the following examples.

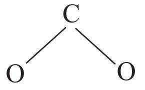
(a) Mono Atomic Molecules: The dipole moment of mono atomic molecule is zero.

(b) Diatomic Molecules: Diatomic molecule are of two types:

(i) Homopolar Molecules: They are symmetrical, so the value of their dipole moment is zero. In such type of molecules the electron pairs binding the atoms are situated equidistant between the constituents of the molecules, e.g., N_2, Cl_2 and H_2.

(ii) Heteropolar Molecules: Such type of molecules have definite dipole moments. This indicates that they may have their covalent electrons undergoing distortion by being drawn nearer to one atom than the other. e.g., Br_2 , I_2 etc.

(c) Tri Atomic Molecules: If the shared electrons in a tri atomic molecule are equidistant from the constituent atoms, the molecule will be non-polar, and of the shared electron in a molecule are not equidistant, a dipole moment would be present and the molecule would be polar. But some times it are not equidistant between the atoms, the molecule as a whole remains non-polar, e.g., carbon dioxide may have either of the following two structures.



Triangular

$$O - C - O$$

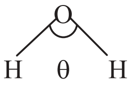
Linear

Since the electrons are drawn towards oxygen atoms, the triangular structure would always make the resultant molecule polar. Hence triangular structure is not possible. But in linear molecule, even if the electron pair is not equidistant between the atoms, the electric moment on one side of the molecule balance the moment on the other side, and the net dipole moment is therefore zero. The carbon dioxide molecule is linear and symmetrical and hence has no dipole moment. Similar in the case with molecules as carbon disulphide, stannic chloride, carbon tetrachloride and the paraffin hydrocarbons (both saturated and unsaturated). Most recent studies have shown that the carbon dioxide has a resonance structures.

$$\overset{+}{O} \underset{=}{\rightarrow} \overset{-}{C} \equiv O \leftrightarrow O = C - O \leftrightarrow O = \overset{-}{C} \underset{=}{\leftarrow} \overset{+}{O}$$

Resonance Structure of Carbon-dioxide

Water has an appreciable value of permanent dipole moment which rules out the possibility of its having a symmetrical linear structure. The molecule is known to have an unsymmetrical or bent triangular structure, the two OH bonds meeting at an angle.



In this form, the molecule possesses two dipole moments which do not cancel each other and give a definite resultant. The bond angle between both O – H bond can be calculated with the help of following formula:

$$\mu = 2m \cos \frac{2}{\theta}$$

where, m = bond moment of each O− H bond

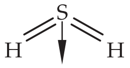
θ = bond angle between the bond

Experimentally it is observed that in H_2O each O – H bond has a moment of 1.60 D and the dipole moment of whole molecule is 1.85 D. Hence, the bond angle between both O – H bond will be

$$1.84 = 2 \times 1.60 \times \cos \frac{\theta}{2}$$

$$\theta = 109^\circ 24'$$

Sulphur dioxide has a dipole moment, which shows that the two oxygen atoms do not lie symmetrically w.r.t. the sulphur atom. It is known to have a bent structure, as shown below and, therefore, exhibits permanent dipole.



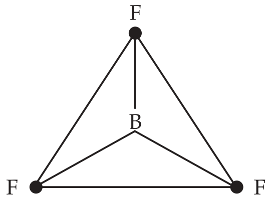
(d) Tetra Atomic Molecules: If the value of dipole moment is zero in tetra atomic molecules, then the shape of the molecule is either trigonal planar or symmetrical planar.

If a tetra atomic molecule shows a definite value of dipole moment, then its geometry is pyramidal, e.g., NH_3, PH_3, AsH_3 etc., where N, P and As is situated at the apex of the pyramid and the hydrogen lie at the other three corners.

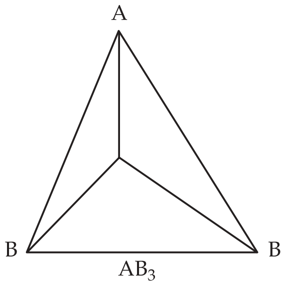
(e) Penta Atomic Molecules: For penta atomic molecules following three geometrical structure are possible:

(a) Tetrahedral	μ = zero, e.g. CCl_4, CH_4
(b) Square planar	μ = zero, e.g. $[Ni(CN)_4]^{2-}$
(c) Pyramidal	μ = have definite value e.g. penterythritole.

Similarly square planar and tetra-hedral model are non-polar, i.e., the value of their dipole moment is zero.



Trigonal Planar



Pyramidal Shap

2.7 OPTICAL ACTIVITY

A beam of ordinary light consists of electromagnetic waves in many planes. When a beam through a polarizer, only wave oscillating in a single plane pass through the emerging beam of light having oscillation in a single plane is said to be plane polarized.

When plane polarized light is passed through certain organic compounds, the plane of polarized light is rotated. A compound that can rotate the plane of polarized light is called optically active, and this property of a compound is called optical activity.

A compound which rotates, the light to the left (anticlock wise) is said to be levorotary, and those who rotates the light to the right (clock-wise) is said to be dextrorotary. By convention rotation to the left is given a minus sign (–) and rotation to the right is given a plus sign (+).

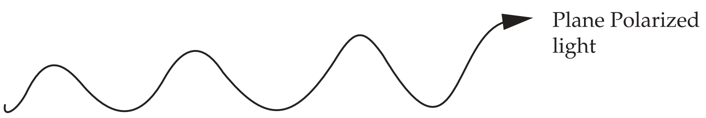


Fig. 2.19 Plane polarized light

2.7.1 Specific Rotation

The rotation of plane polarized light is an intrinsic property of optically active molecules. When a polarized beam of light is passed through the solution of an optically active compound, its plane is rotated through an angle "α" (angle of rotation). This rotation depends on the number of optically active molecules encountered. Therefore, α is proportional to both the concentration and the length of the sample solution.

The specific rotation, which is characteristic of an optically active substance, is expressed as

$$[\alpha] = \frac{\alpha}{l \times c}$$

where, $[\alpha] =$ Specific rotation in degree

$d =$ observed angle of rotation in degree

$l =$ length of the sample solution in decimeter

$c =$ concentration of the sample solution in g/ml

Thus, the specific rotation can be defined as the observed angle of rotation at a concentration of 1 g/ml and path length of 1 dm. Conventionally, a specific rotation is reported as $[\alpha]_{\mathrm{D}}^{t}$, where "*t*" stands for temperature and "D" for *D* line of sodium used for determination.

2.7.2 Measurement of Optical Activity

Optical activity is measured with the help of polarimeter. It is basically a system of polarizers with a sample tube placed in-between. At first fills the sample tube with the help of an optically inactive medium (air or solvent), and pass the polarized sodium light (emerging from the polarizer) through it. The analyzer is then turned to established a dark field. This gives a zero reading on the circular scale around the analyzer. Now the solution of the given optically active compound is placed in the sample tube. The plane of polarized light passing through is rotated. The analyzer is turned to re-establish the dark field. The angle of rotation $[\alpha]$ is noted in degree on the circular scale. The specific rotation is calculate using the above expression.

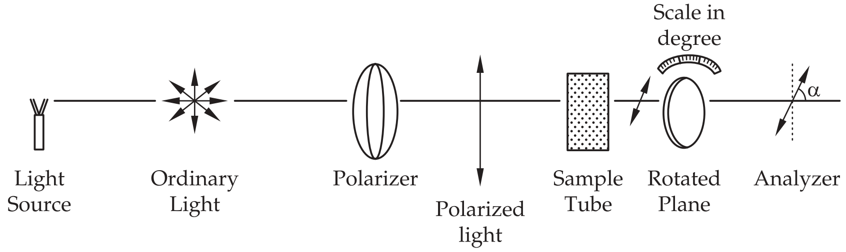


Fig. 2.20 Schematic Diagram of a polarimeter.

NUMERICAL PROBLEMS

Prob. 2.1 *The radius of a given capillary is 0.0335 cm. A liquid whose density is 0.866 gm/cm^3 rises to a height of 2.00 cm in the capillary when it is dipped in the liquid. Calculate the surface tension of the liquid.*

Solution. Since

$$\gamma = \frac{1}{2} rhdg$$

Here, $r = 0.0335$ cm, $h = 2.0$ cm

$d = 0.866$ gm/cm^3 and $g = 981$

Therefore, $\gamma = \frac{1}{2} \times 0.0335 \times 2.0 \times 0.866 \times 981$

$$= 28.45$$

Thus surface tension of the liquid is 28.45 dynes/cm. Ans.

Prob. 2.2 *At 20°C the surface tension of chloroform is 16.2 dynes/cm. The density of liquid and gas at the same temperature are 0.9188 gm/cm*^{2} *and 0.0110 gm/cm*^{3}*. If the radius of the capillary is 0.105 mm. What would be the height of liquid in capillary, angle of contact being zero.*

Solution. $\gamma = \frac{1}{2}\left(h + \frac{r}{3}\right)(d_l - d\theta)\ gr$

Here, $\gamma = 16.2,\ h = ?$

$d_l = 0.9188,\ d\theta = 0.0110$

$g = 981$ and $r = 0.0105$ cm

Substituting these values

$$16.2 = \frac{1}{2}\left(h + \frac{0.0105}{3}\right)(0.9188 - 0.0110)\ 981 + 0.0105$$

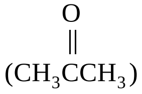
or $h = 3.46$

Thus, the liquid rises to height of 3.46 cm in the capillary. Ans.

Prob. 2.3 *At 20°C the density of acetone is 0.7190. If the parachor value of carbon, hydrogen, oxygen and C = O is 7.2, 16.2, 20.0 and 23.2 respectively, then find out the surface tension of acetone.*

Solution. We know that

$$P = M\gamma^{1/4}D$$

The molecular weight of acetone  $(CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3)$ is

$$= 15 + 12 + 16 + 15$$

$$= 58$$

Density $D = 0.791$

$$[P] = 3C + 6H + 1[O] + 1 \text{ double bond}$$

$$= 3 \times 7.2 + 6 \times 16.2 + 1 \times 20 + 23.2 \times 1$$

$$= 21.6 + 97.2 + 20 + 23.2$$

$$= 162$$

By putting the value of P, M, γ and D in equation (i)

$$\frac{58}{0.791} \times \gamma^{1/4} = 162$$

$$\gamma^{1/4} = \frac{162 \times 0.791}{58}$$

$$\gamma = \left(\frac{162 \times 0.791}{4}\right)^4$$

$$= (2.209)^4$$

$$= 23.81$$

So the surface tension of acetone is 23.81.

Prob. 2.4 *The time of flow of water through an Ostwald's viscometer is 1.52 minutes, for the same value of an organic liquid of density 0.800 gm/cc, it is 2.25 mintues. Find the viscosity of the liquid relative to that of water and also absolute viscosity at 20°C. Density and viscosity of water at 20°C are 1 gm/cc and 1.002 × 10*$^{-2}$ *Poise respectively.*

Solution. Since $\frac{n_1}{n_2} = \frac{t_1\, d_1}{t_2\, d_2}$

(i) To determine viscosity of the liquid relative to that of water.

Here, $t_1 = 1.52$ min, $d_1 = 1.0$ gm/cc

$t_2 = 2.25$ and $d_2 = 0.800$ gm/cc

$$\therefore \qquad \frac{n_1}{n_2} = \frac{1.0 \times 1.52}{0.8 \times 2.25} = \frac{1.52}{1.8} \text{ or } \frac{0.84}{1.0}$$

or $n_1 : n_2 :: 0.844 : 1.0$

(ii) To determine absolute viscosity at 20°C

Since viscosity of water at $20°\text{C} = 1.002 \times 10^{-2}$ Poise

$$n_1 = n_2 \frac{d_1\, t_1}{d_2\, t_2}$$

n_1 = viscosity of liquid

n_2 = viscosity of water

$$= \frac{1.002 \times 10^{-2} \times 0.8 \times 2.25}{1.0 \times 1.52}$$

$$\mathbf{= 1.187 \times 10^{-2}\ Poise}$$ **Ans.**

Prob. 2.5 *A steel ball of density 7.99 gm/cc, and a diameter of 4 mm requires 53 seconds to fall a distance of 1 meter through an oil of density 1.10 gm/cc. Calculate the viscosity of oil in Poise.*

Solution. $n = \frac{2r^2 (d_s - d_l)\, g}{9l / t}$

Here, $r = 0.2$ cm

$d_s = 7.99$ gm/cc

$d_l = 1.10$ gm/cc

$l = 100$ cm

$$t = 53 \text{ seconds}$$

and $$g = 980$$

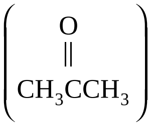
Now substituting the various values

$$n = \frac{2\times(0.2)^2(7.99-1.1)\,980}{9\times100/53}$$

$$\mathbf{= 31.39\ Poise}$$ **Ans.**

Prob. 2.6 *The density of acetone is 0.791 at 20°C. If the parachor value of C, H and > C = O bond is 7.2, 16.2, 20.0 and 23.2 respectively, then find out the surface tension of acetone.*

Solution. $\mathrm{P} = \dfrac{\mathrm{MY}^{1/4}}{\mathrm{P}}$

The molecular mass of acetone  $\left(\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{CH_3CCH_3}}\right)$ is

$$= 15+12+16+15$$

$$= 58$$

Density, $P = 0.791$

$$[\mathrm{P}] = 3\mathrm{C}+6\mathrm{H}+1[\mathrm{O}]+1 \text{ double bond}$$

$$= 3\times7.2+6\times16.2+1\times20+23.2$$

$$= 21.6+97.2+20+23.2 = 162$$

Now put the value of P, M, γ and p in above equation

$$\frac{58}{0.791}\times\gamma^{1/4} = 162$$

$$\gamma^{1/4} = \frac{162\times0.791}{58}$$

$$\gamma = \left(\frac{162\times0.791}{58}\right)^4$$

$$= (2.209)^4$$

$$\mathbf{= 23.81}$$ **Ans.**

Prob. 2.7 *Suppose at 0°C from a stalognometer we obtain 60 and 182 drops of water and ether respectively. The density of water and ether is 0.998 and 0.712 gm/cm^2 respectively. If the surface tension of water is 72 dynes/cm, then find out the surface tension of ether.*

Solution. Surface tension of water $\gamma_1 = 72$ dynes/cm

Surface tension of ether $\gamma_2 = ?$

Number of water drop $n_1 = 60$

Number of ether drop $n_2 = 182$

Density of water $d_1 = 0.998$ gm/cm^3

Density of ether $d_2 = 0.712$ gm/cm^3

Put these values in following equation

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2\, d_1}{n_1\, d_2}$$

$$\frac{72}{\gamma_2} = \frac{182 \times 0.998}{60 \times 0.712}$$

$$\gamma_2 = \frac{72 \times 60 \times 0.712}{182 \times 0.998}$$

= 16.93 *dynes/cm* **Ans.**

EXERCISES

Subject Questions

2.1 What do you understand by surface tension of a liquid? What are its units and dimensions? Give one experimental method for its determination.

2.2 Define coefficient of viscosity. How does it vary with temperature changes.

2.3 Define parachor and discuss its use in the elucidation of molecular structure.

2.4 Give one method for the determination of viscosity of a liquid.

2.5 Describe in detail the Abbe refractormeter for the determination of refractive index of a liquid.

2.6 Explain the term dipole moment. Discuss some of its applications.

2.7 What information can dipole moment, given about the structure of the molecule?

2.8 Explain the term refractive index. How is it determined experimentally?

Objective Questions

2.1 The equation of parachor is:

(a) (M/D) $r^{1/8}$ (b) (M/D) $r^{1/2}$

(c) (M/D) $r^{1/6}$ (d) (M/D) $r^{1/4}$

2.2 Which molecule have zero dipole moment:

(a) H_2O (b) SO_2

(c) CS_2 (d) H_2S

2.3 The unit of dipole moment is:

(a) dynes/cm (b) Poise

(c) dynes/cm^2 (d) debye

2.4 The unit of viscosity is:

(a) dyne cm^{-2} time (b) dyne cm^2 time^{-1}

(c) dyne cm^2 time (d) dyne cm^1 time^{-1}

2.5 Viscosity is related with:

(a) parachor (b) surface tension

(c) rheychor (d) none of these

2.6 The maximum viscosity of a liquid in:

(a) water (b) glycol

(c) acetone (d) ethanol

2.7 Parachor is a:

(a) additive property (b) additive and constitutive

(c) constitutive (d) none of these

2.8 The value of debye is:

(a) 10^{-8} esu (b) 10^{-10} esu $\times$ cm

(c) 10^{-18} esu $\times$ cm (d) 10^{-7} esu

2.9 Which one is a colligative property:

(a) molecular weight (b) osmotic pressure

(c) parachor (d) surface tension

2.10 The experimental parachor value for benzene is:

(a) 107 (b) 206.2

(c) 236 (d) 307

ANSWERS

2.1 (d) **2.2** (b) **2.3** (d) **2.4** (a) **2.5** (c) **2.6** (b)

2.7 (b) **2.8** (c) **2.9** (b) **2.10** (b)