

## 4.2 INTRODUCTION

As you have studied in the previous unit (i.e. unit 3), liquids can be obtained from gases by cooling the latter below their respective critical temperature followed by the treatment of high pressure. Effect of cooling is to decrease the thermal energies of molecules and the effect of pressure is to decrease the volume of the system so as to allow the molecules to come closer, thereby increasing the force of attraction amongst them. Alternatively, liquids can be obtained by heating solids upto or beyond their melting points. Thus we see the properties of liquids lie in between those of solids and gases. For example liquids are less compressible than gases but a little more compressible than solids. They are less dense than solid but more dense than gases. The two important properties of liquids, namely, the fixed volume but no fixed shape arises mainly because of the following two facts

- (1) The energies binding the molecules are larger than their average thermal energy.
- (2) Their binding energies are not strong enough to stop the motion of the molecules altogether, as in the case of solids, with the result that molecules can move from one place to another but cannot escape from the liquid unless they are present at the surface.

## 4.3 INTERMOLECULAR FORCES

Since the molecules in a liquid are not far apart from each other, the intermolecular forces are fairly strong. The characteristic properties of liquid arise from the nature and the magnitude of these intermolecular forces.

Intermolecular forces in liquids are collectively called von der Waal's forces. These forces are essentially electrical in nature and result from the attraction of charges of opposite sign. The principle kinds of intermolecular forces are:

- (i) Dipole-dipole interaction
- (ii) London forces
- (iii) Hydrogen bonding.

### 4.3.1 Dipole-dipole interaction

We have seen that HCl is an example of a polar molecule. Such molecule have a partial positive charge at one end and a partial negative charge at the other.

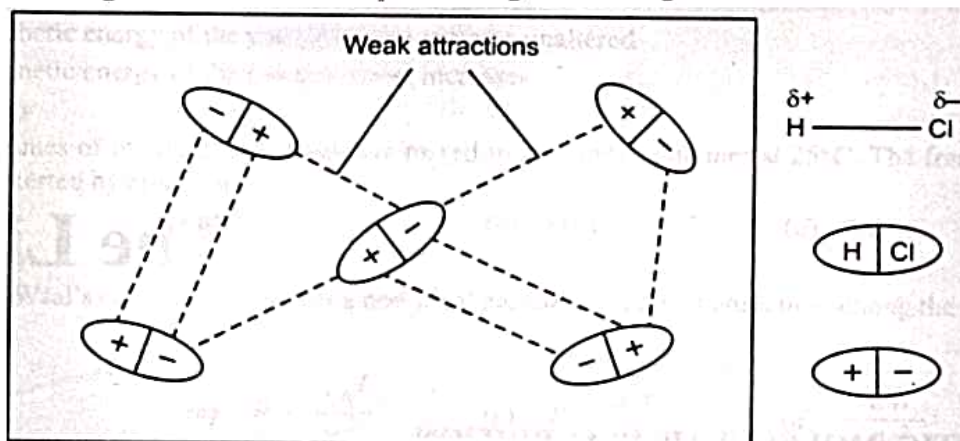


Fig 4.1 Weak attraction between polar HCl molecules

They are called dipoles. The positive end of one dipole attracts the negative end of the other. The thermal energy of molecules tends to disturb these attractions but still there exists a net attraction between the polar molecules. These forces are referred to as dipole-dipole attractions. Generally such attractions are about 1% as strong as covalent bond. It is to be noted that the attractions between the opposite poles are greater than repulsive forces between like poles. Thus these molecules have a net attraction to each other.

### 4.3.2 London forces

In 1930 Fritz London first offered a simple explanation of weak forces between nonpolar molecules or atoms. In a molecule (or atom) electrons are constantly moving. Most of the time electrons in the molecules could not be visualized as distributed symmetrically. However according to the principle of probability, for an instant the electrons may concentrate on one side of the molecule than the other. This causes the molecule (A) to become momentarily polar and we call it instant dipole.

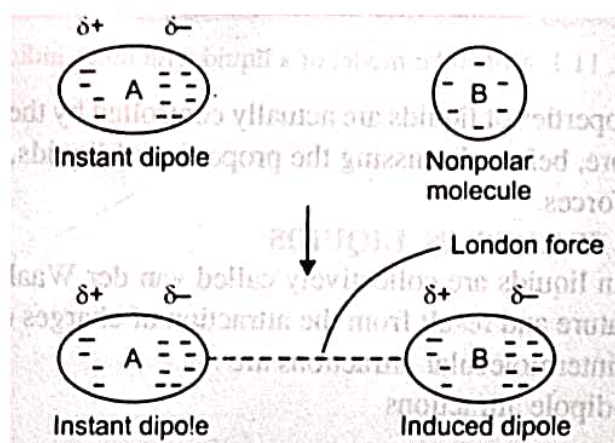


fig 4.2 Explanation of London forces

The negative side of the instantaneous dipole repels the electrons of an adjacent molecule (B). As a result the second molecule B also becomes a dipole by induced polarity. This is called induced dipole **Fig 4.2**.

The instantaneous dipole A and the induced dipole B will now attract each other. Because the electrons keep moving an instant dipole may vanish the next moment and new are produced. This continual process produces a weak overall attraction between molecules of liquid.

The momentary attraction between the molecules of liquid caused by instantaneous-dipole and **induced-dipole attractions are called London forces**. These London forces are present in polar molecules also in addition to other von der Waal's forces.

The strength of the London forces depends as to how easily the electron cloud in a particular molecule is deformed. This is determined by the number of electrons and also on the size of the molecule. Thus Argon ( $-245.9^{\circ}\text{C}$ ) with a greater number of electron and larger molecular weight has a higher boiling point than helium ( $-268.9^{\circ}\text{C}$ ).

### 4.3.3 Hydrogen bonding

In compounds of hydrogen with strongly electronegative elements, such as fluorine, oxygen and nitrogen, the electron pair shared between the two atoms lies far away from the hydrogen atom as a result of which the hydrogen atom becomes highly electropositive with respect to other atom which become electronegative. This phenomenon of charge separation

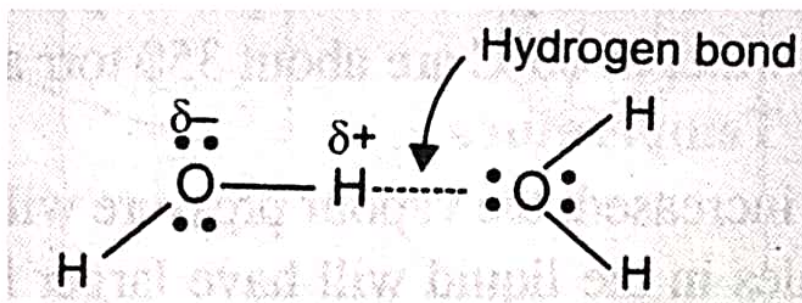
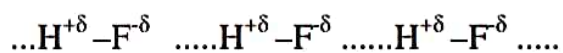


Fig 4.3 Hydrogen bond

in water is represented as shown in the fig 4.3. The electronegativity difference in H and O is so large that the electron pair in the covalent bond, H-O is shifted toward O. It leaves a partial positive charge on the H atom. This leads to a strong electrostatic attraction between positively charged H atom and an unshared electron pair on the O atom of another molecule. Thus you can understand that two or more molecules may associate together to form large cluster of molecule. This is shown below for the association of several molecules of hydrogen fluoride.



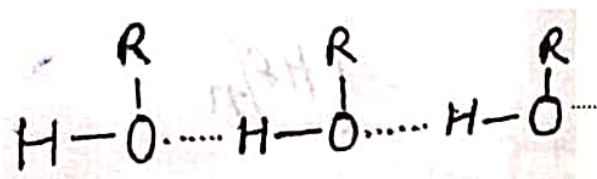
In this case, while the length of covalent bond between H and F atoms is found to be  $1.00\text{\AA}$ , the length of the hydrogen bond between H and F atoms of neighbouring molecules has been found to be  $1.55\text{\AA}$ . this cluster of HF molecules may be described as  $(\text{HF})_n$

**The attractive force which binds hydrogen atom of one molecule with electronegative atom of another molecule, generally of the same substance is known as the hydrogen bond.**

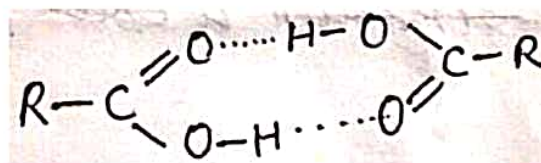
The hydrogen bonding is the strongest of all intermolecular forces including the dipole-dipole attractions and London forces.

In the above discussion you have seen that cluster of HF molecule is described as  $(\text{HF})_n$  and cluster of water molecule may be described as  $(\text{H}_2\text{O})_n$

Alcohols and carboxylic acids also form associated molecules for the same reason, as shown below



Alcohols



Carboxylic Acids

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## ***4.4 STRUCTURE OF LIQUIDS***

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In a liquid, the molecules are not as rigidly fixed as in a solid. They have some freedom of motion which, however, is much less than that in a gas. Liquids resemble solids in being compact, incompressible and in having a definite volume. These properties are indicative of a regular structure in liquids similar to that in solids.

From X-ray diffraction technique, it has been found that the resemblance of liquid state with solid state is valid within a small range; i.e. within only a small distance from a given molecule. In other words the regularly ordered structure which exists in crystalline solids is of short range in liquids. It means it exists only within a short distance from any given molecule. A solid possesses short range as well as long range order since the ordered structure extends regularly throughout the whole crystal.

Now it should be clear to you that

- (i) A gas consists of molecules separated wide apart in empty space. The molecules are free to move about throughout the container.
- (ii) A liquid has molecules touching each other. However, the intermolecular spaces permit the movement of molecules throughout the liquid.
- (iii) A solid has molecules, atoms or ions arranged in a certain order in fixed positions in the crystal lattice. The particles in a solid are not free to move about but vibrate in their fixed positions.

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## ***4.5 CHARACTERISTIC PROPERTIES OF LIQUIDS***

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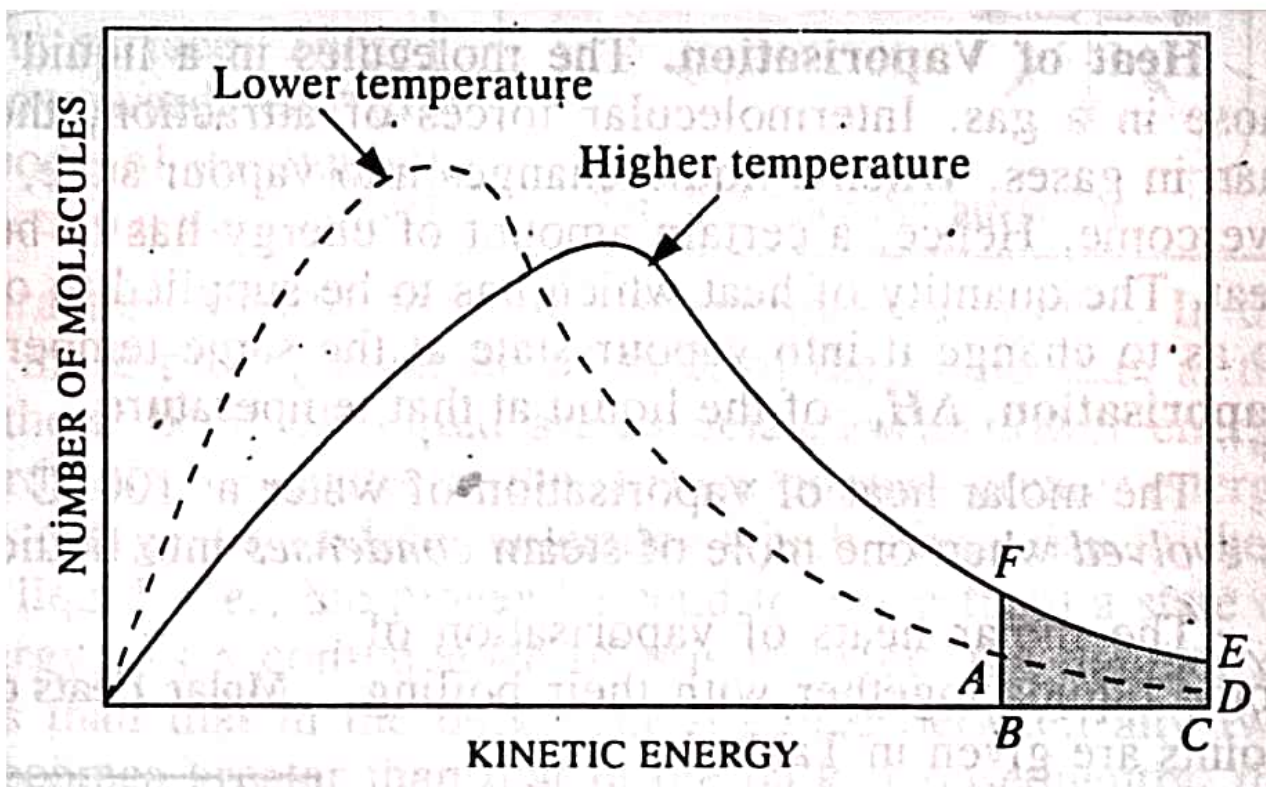
As you have studied earlier in this unit that the properties of liquids arise from

- (i) The nature and
- (ii) The magnitude of intermolecular forces of attraction existing between their molecules. The important properties of liquids are
  1. Vapour pressure
  2. Surface tension
  3. Viscosity
  4. Refraction

Now you will study these properties in detail

### **4.5.1 Vapour pressure**

When a liquid is in an open vessel, it evaporates. You have studied in the gases unit, that the gas molecules have a particular velocity. This is so in the case of liquids also. Only a few liquid molecules have lower or higher velocity, i.e. lower or higher kinetic energies. The energy distribution of molecules in a liquid is shown in Fig 4.4.

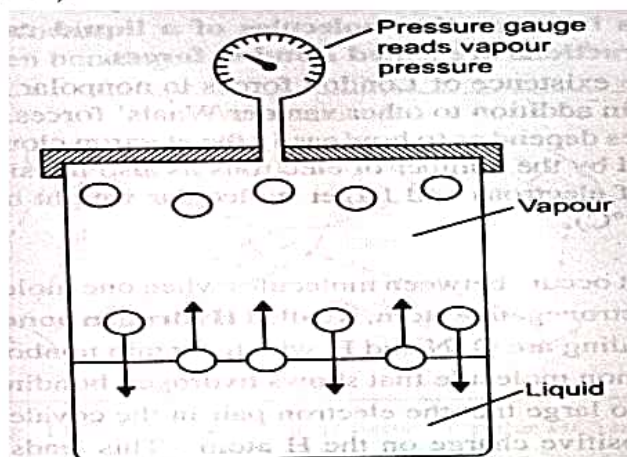


**Fig 4.4 energy distribution of molecules of a liquid**

It is clear from the Fig 4.4 that the number of molecules with high kinetic energies, as shown by the shaded portion ABCD of the dotted curve is very small. This number, however, increases with rise in temperature, as shown by the shaded portion FBCE of the bold line curve.

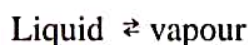
When a liquid is placed in an open vessel it evaporates. The molecules in the liquid are moving with different kinetic energies. The molecules that possess above average kinetic energies can overcome the intermolecular forces that hold them in the liquid. These energetic molecules escape from the surface as vapour. This process by which molecules of a liquid go into gaseous state is called vaporisation or evaporation. The reverse process whereby gas molecules become liquid is called condensation.

When a liquid is placed in a closed vessel, the molecules with high kinetic energies escape into space above the liquid as shown in fig 4.5. As the number of molecules in the gas phase increases, some of them strike the liquid surface and are recaptured (condensation).



**Fig 4.5 Illustration of vapour pressure**

A stage comes when the number of molecules escaping from the liquid is equal to the number of molecules returning to the liquid. Thus a dynamic equilibrium is established between the liquid and the vapour at a given temperature.



Now the concentration of the vapour in the space above the liquid will remain unchanged with lapse of time. Hence the vapour will exert a definite pressure at the equilibrium. Hence vapour pressure of a liquid defined as:

**The pressure exerted by the vapour in equilibrium with the liquid at a fixed temperature is the vapour pressure of the liquid.**

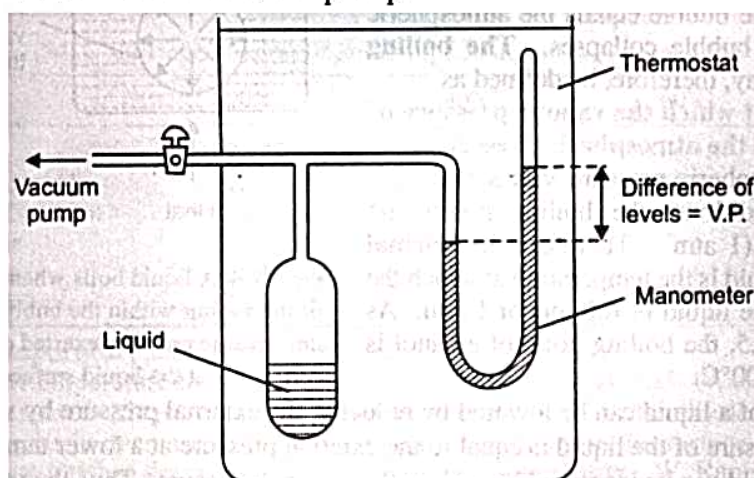
As the temperature rises, the number of molecules escaping from the liquid surface increases as there is an increase in the number of vapour molecules in the space above the liquid when equilibrium is attained.

Hence vapour pressure of the liquid increases with increase of temperature.

#### 4.5.1.1 Determination of vapour pressure

##### (a) Static method:

A simple apparatus used in this method is shown in fig 4.6. A sufficient amount of the liquid whose vapour pressure is to be determined is placed in the bulb connected to a mercury manometer and a vacuum pump.

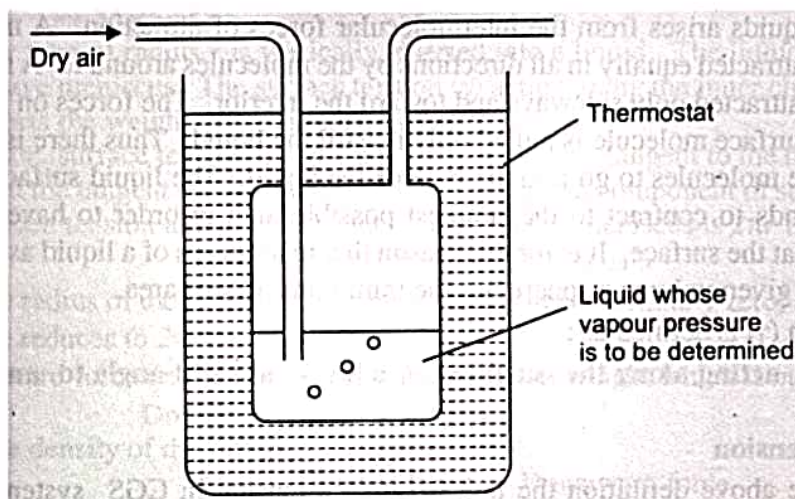


**Fig 4.6 Determination of vapour pressure by static method**

All the air from the bulb is removed by working the vacuum pump and the stopcock closed. A part of liquid evaporates. The system is then maintained at a fixed temperature for enough time so that equilibrium is attained. The difference in the levels of mercury in the manometer is equal to vapour pressure of the liquid. This method is used for liquids having vapour pressure up to one atmosphere.

##### (b) Dynamic method:

The apparatus used for the dynamic method is shown in fig 4.7.



**Fig 4.7 Dynamic method**

An inert gas is passed through the given liquid at a constant temperature (T). The gas saturated with the vapour of the liquid leaves the flask at the exit tube. If V is the volume of the gas passed and m the loss in weight of the liquid the vapour pressure is given by the expression.

$$\text{Vapour pressure} = \frac{m}{MV} RT$$

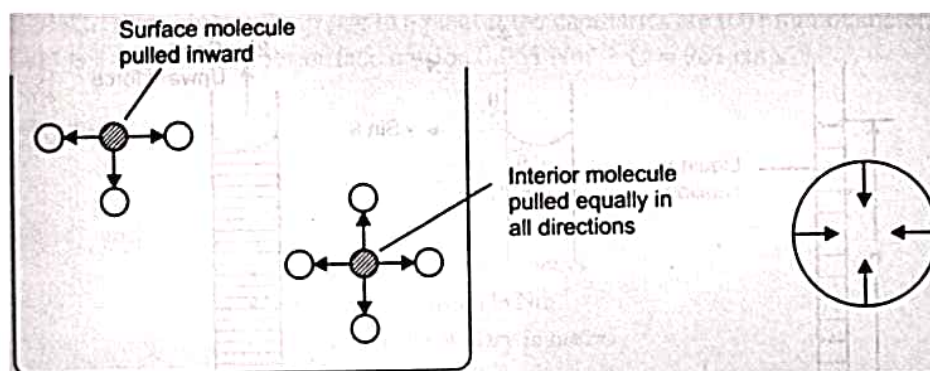
Where M is the molecular weight of the liquid and R the gas constant. This method is particularly useful for liquids of very low vapour pressure

### 4.5.2 Surface tension

The existence of strong intermolecular forces of attraction in liquids gives rise to a property known as surface tension. The phenomenon of surface tension can be described as follows.

A molecule in the interior of a liquid is attracted equally in all directions by the molecules around it. A molecule in the surface of a liquid is attracted only sideways and towards the interior. The forces on the sides being counterbalanced, the surface is pulled only inward the liquid. These unbalanced attractive forces acting downward tend to draw the surface molecules into the body of the liquid and, therefore, tend to reduce the surface to minimum. The liquid then behaves as if it were under a strain or tension. It is this force which is called surface tension. It may be defined as **“the force in dynes acting on the surface of the liquid at right angles to one centimetre length of the surface”**. It is represented by a symbol  $\gamma$  (gamma).

In CGS system the unit of surface tension is dynes per centimetre ( $\text{dyne cm}^{-1}$ ). In SI system, the unit is Newton per metre ( $\text{Nm}^{-1}$ ). Both these units are related as follows



**Fig 4.8 molecular attractions**

$$\text{Surface energy} = \frac{\text{amount of work done}}{\text{amount of area extended}} = \frac{\text{force} \times \text{distance}}{\text{area}}$$

Hence in CGS units we have

$$\text{Surface energy} = \frac{\text{dyn} \times \text{cm}}{\text{cm}^2} = \text{dyn} \times \text{cm}^{-1} = \text{surface tension}$$

In SI units we have

$$\text{Surface energy} = \frac{\text{N} \times \text{m}}{\text{m}^2} = \text{Nm}^{-1}$$

obviously,

$$1 \text{ dyne cm}^{-1} = (10^{-5}\text{N}) (10^{-2}\text{m})^{-1} = 10^{-3}\text{Nm}^{-1}$$

### 4.5.2.1 Effect of temperature on surface tension

When temperature increases, there is increase in kinetic energy of liquid molecules ( $KE \propto T$ ) thereby decreasing intermolecular forces. It results in decrease in inward pull functioning on the surface of the liquid. That means you can say surface tension decreases with increase in temperature. As surface tension arises of the attractive forces operating between the molecules, Ramsay and Shields gave the following relationship between the surface tension of a liquid and its temperature.

$$\gamma(M/d)^{2/3} = k(t_c - t - 6)$$

where k is constant

$t_c$  is critical temperature and t any other temperature  $\gamma (M/d)^{2/3}$  represents molar surface energy of liquid.

### 4.5.2.2 Determination of surface tension

#### (i) Capillary rise method:

In this method a capillary tube of radius r is vertically inserted into the liquid. The liquid rises to a height h and form a concave meniscus.

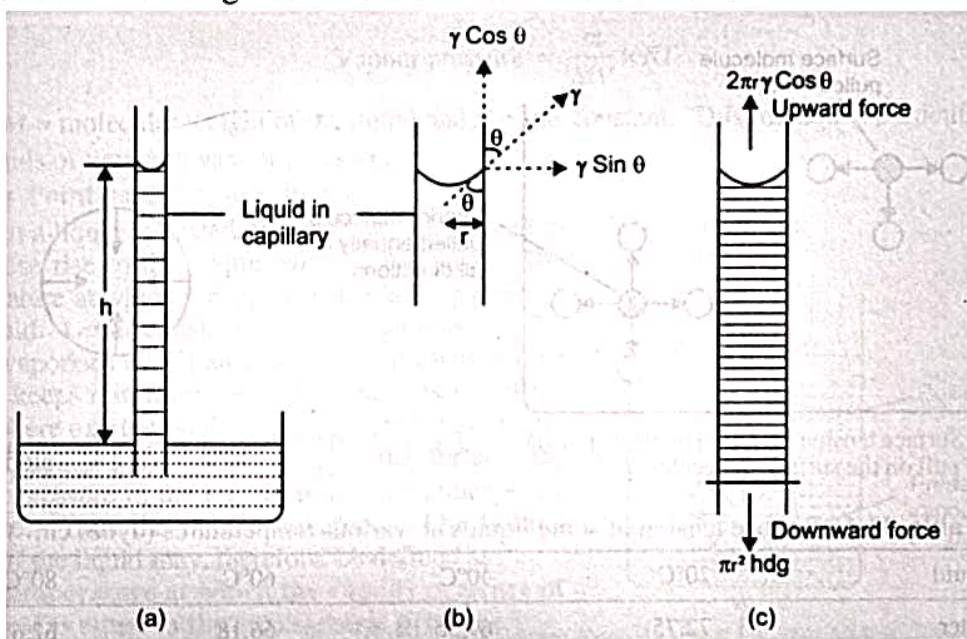


Fig 4.9 capillary rise method of surface tension



The surface tension  $\gamma$  acting in the inner circumference of the tube exactly supports the weight of the liquid column. By definition, surface tension is force per 1 cm acting at a point tangent to the meniscus surface. If the angle between the tangent and the tube wall is  $\theta$ , then the vertical component of surface tension is  $\gamma \cos\theta$ . The total surface tension along the circular contact line of meniscus is  $2\pi r$  times.

Therefore upward force =  $2\pi r\gamma \cos\theta$

Where  $r$  is radius of capillary. For most liquids,  $\theta$  is essentially zero, and  $\cos\theta = 1$ , then the upward force reduces to  $2\pi r\gamma$

The downward force on the liquid column is due to its weight which is mass  $\times$   $g$ , thus downward force is  $h\pi r^2 dg$ , where  $d$  is density of the liquid

Now upward force = downward force

$$2\pi r\gamma = h\pi r^2 dg$$

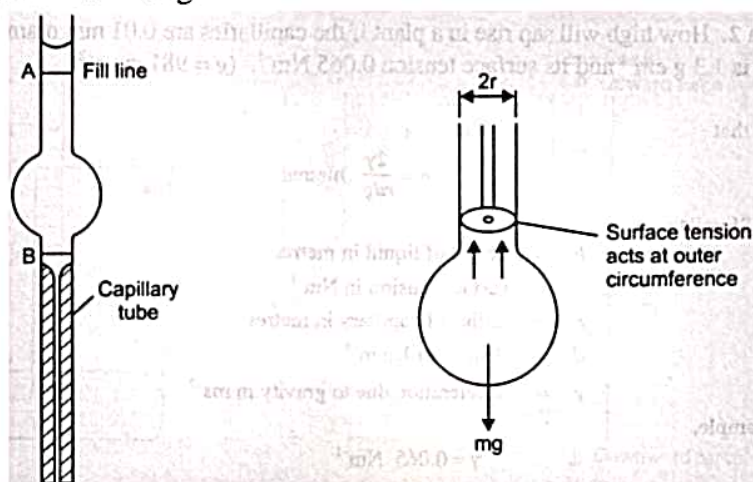
$$\gamma = hrdg/2 \text{ dynes/cm}$$

once  $r$ ,  $h$  and  $d$  are known  $\gamma$  can be calculated.

(ii) **Drop weight/ number method:**

When a liquid is allowed to flow very slowly through a capillary tube a drop will form which will increase upto a certain point and then fall. If the radius of the end of the tube be  $r$ , the total surface tension supporting the drop will be  $\gamma 2\pi r$ . The drop falls down when its weight  $W$  is just equal to this force. Hence we have

$$\gamma 2\pi r = W = mg$$



**Fig 4.10** determination of surface tension by drop-pipette

The apparatus employed is a glass pipette with a capillary at the lower part. This is called a drop pipette or stalagmometer. It is cleaned, dried and filled with the experimental liquid, say upto the mark A. (Fig 4.10). Then the surface tension is determined by any of the following two methods.

(a) **Drop weight method:**

About 20 drops of the given liquid are received from the drop-pipette in a weighing bottle and weighed. Thus weight of one drop is found. The drop-pipette is again cleaned and dried. It is filled with the second reference liquid (say water) and weight of one drop is determined as before.

Then we have

$$m_1 g = 2\pi r \gamma_1 \text{ and } m_2 g = 2\pi r \gamma_2$$

$$\gamma_1/\gamma_2 = \frac{m_1}{m_2}$$

Thus knowing the surface tension of one liquid, the surface tension of other liquid can be found.

**(b) Drop number method:**

The drop pipette is filled up to the mark A with the liquid whose surface tension is to be determined. The numbers of drops are counted as the meniscus passes from A to B. Similarly the pipette is filled with the reference liquid as the meniscus passes from A to B. Let  $n_1$  and  $n_2$  be the number of drops produced by the same volume  $V$  of the two liquids. Thus,

the volume of drop of the experimental liquids =  $V/n_1$

mass of one drop of this liquid =  $V/n_1 \times d_1$

where  $d_1$  is its density.

Similarly the mass of one drop of reference liquid =  $V/n_2 \times d_2$

Then we have 
$$\gamma_1/\gamma_2 = \frac{(V/n_1)d_1}{(V/n_2)d_2} = \frac{n_2 d_1}{n_1 d_2}$$

The density  $d_1$  can be determined by density bottle, once  $\gamma_2$  and  $d_2$  are known  $\gamma_1$  can be calculated.

For most liquids surface tension at room temperature vary between 27 and 42 dynes  $\text{cm}^{-1}$ . For water however,  $\gamma$  is 72.8 dynes  $\text{cm}^{-1}$  at 20°C.

This high value is obviously due to strong intermolecular forces which exists in water as a result of extensive hydrogen bonding.

**4.5.2.3 Surface tension and chemical constitution**

From the study of a large number of liquids, Maclead (1923) showed that

$$\frac{\gamma^{1/4}}{D-d} = C \quad \text{.....(1)}$$

Where  $\gamma$  is surface tension of the liquid,  $D$  its density and  $d$  density of vapour at the same temperature,  $C$  is a constant. Sugden (1924) modified this equation by multiplying both sides by  $M$ , the molecular weight of the liquid

$$M \cdot \gamma^{1/4} / D-d = MC = [P] \quad \text{.....(2)}$$

The quantity  $P$ , which is a constant for a liquid, was given the name parachor. As  $d$  is negligible as compared to  $D$  equation (2) reduces to

$$\begin{aligned} M\gamma^{1/4}/D &= [P] \\ \text{or } M/D\gamma^{1/4} &= [P] \\ V\gamma^{1/4} &= [P] \quad \text{.....(3)} \end{aligned}$$

Where  $\gamma$  is molar volume of the liquid. If surface tension  $\gamma$  is unity then  $V = [P]$   
Thus parachor may be defined as the molar volume of a liquid at a temperature at which its surface tension is unity.

**Use of parachor in elucidating molecular structure:**

Sugden examined the experimental parachor values of several organic compounds of known molecular structure. He showed that parachor is both additive and constitutive property. That is parachor of an individual compound can be expressed as sum of

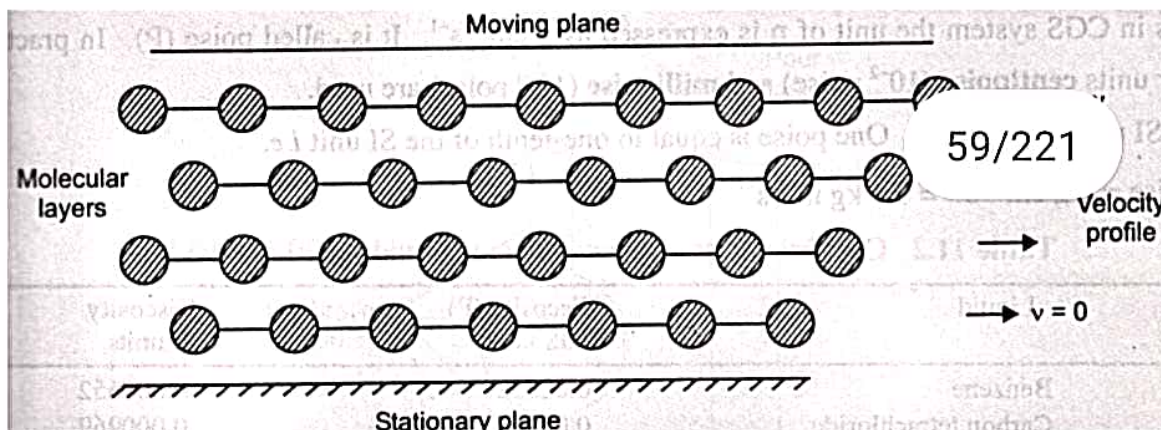
### 4.5.3 Viscosity

Some liquids flow more rapidly than others. In other words, liquid molecules pose resistance to the flow of one layer over the other. This property of liquids which determines their flow is termed viscosity. The property of the liquid which determines its flow is called viscosity of the liquid.

The resistance to flow of one layer of liquid molecules over another depends on the following factors.

1. The intermolecular attractive forces do not permit a free flow of molecules in a liquid. The strength of intermolecular forces gives a rough major of the viscosity of the liquids.
2. The molecular weight or mass of the molecules of a liquid also determines flow of the liquid. Thus heavier the molecule of a given liquid the greater will be its viscosity.
3. Structure and shape of the molecules of a liquid place an important role in influencing its viscosity. Liquids with the large irregularly shaped molecules are generally known to be more viscous than those with small and symmetrical molecule. Since only hard symmetrical molecules have perfectly elastic collision, the large and irregular molecules will have less elastic molecules amongst themselves. Thus collisions between large molecules involves the loss of kinetic energy and as a consequence the intermolecular forces dominating the molecules tends to stick together. This increases the viscosity of the liquid.

4. An increase in temperature decreases the viscosity of the liquid, the molecular motion increases at the expense of cohesive forces causing resistance to flow.
5. The increase of pressure goes to strengthen the cohesive forces between molecules. Hence with increase of pressure the viscosity of a given liquid increases somewhat. The flow is a characteristic property of liquids. Let us consider flow of a liquid. A liquid may be considered to be consisting of molecular layers arranged one over the other. When shearing force is applied, it flows.



**Fig 4.13 flow of liquid on a glass surface**

However the force of friction between the layers offers resistance to this flow. Viscosity of a liquid is a measure of its frictional resistance.

Let us examine a liquid flowing on a glass surface. The molecular layer in contact with the stationary surface has zero velocity. The successive layers above it move with increasingly higher velocities in the direction of the flow.

Now consider two adjacent moving layers of a liquid (fig 4.11). Let these be separated by a distance  $dx$  having velocity difference  $d v$ . The force of friction ( $F$ ) resisting the relative motion of the two layers is directly proportional to the area  $A$  and velocity difference  $d v$ , while it is inversely proportional to the distance between the layers  $dx$ .

$$\begin{aligned} \text{Hence} \quad F &\propto A \, d v / dx \\ &= \eta \, A \, d v / dx \\ \text{or} \quad \eta &= F / A \times dx / d v \end{aligned}$$

where  $\eta$  (eta) is the proportionality constant. It is known as coefficient of viscosity or simply viscosity of a liquid. It may be defined by the above equation as:

the force of resistance per unit area which will maintain unit different of velocity between two layers which are unit distance apart.

**Unit of viscosity:**

$$\begin{aligned} \eta &= F / A \times dx / d v \\ &= \text{force/area} \times \text{distance/velocity} \\ &= \text{mass} \times \text{length} \times \text{time}^{-2} / \text{length}^2 \times \text{length/length/time} \\ &= \text{mass} \times \text{length}^{-1} \times \text{time}^{-1} \end{aligned}$$

In CGS system the unit of  $\eta$  is expressed as  $\text{g cm}^{-1}\text{s}^{-1}$ , it is called poise. In practice smaller units centipoise ( $10^{-2}$  poise) and millipoise ( $10^{-3}$  poise) are used.

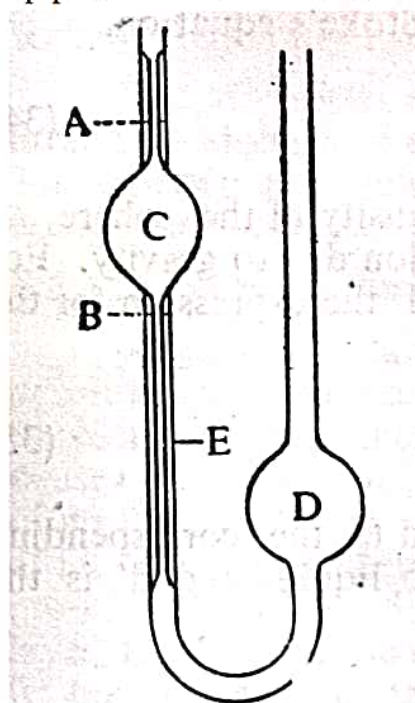
A liquid is said to have coefficient of viscosity as one poise when a force of one dyne maintains a velocity difference of one centimetre per second between two parallel layers of the liquid one cm apart and have an area of contact equal to one square cm. **The reciprocal of viscosity is known as fluidity.**

#### 4.5.3.1 Effect of temperature on viscosity

As the temperature increases, the molecular motion increases at the expense of cohesive forces causing resistance to flow. Therefore, the viscosity of liquids is found to decrease by 1 to 2 per cent for each degree rise of temperature.

#### 4.5.3.2 Determination of viscosity

The apparatus used for determination of viscosity in the laboratory is known as Ostwald's viscometer. A simple form of Ostwald viscometer is shown in fig 4.14, the left-hand limb is essentially a pipette with two calibration marks A and



**Fig 4.14 Ostwald viscometer**

B. A length of capillary tube joins the pipette to the bulb D in the right-hand limb.

A definite volume of liquid (say about 25 ml) is poured into the bulb D with a pipette. The liquid is sucked up near to the top of the left-hand limb with the help of rubber tubing attached to it. The liquid is then released to flow back into the bulb D. The time  $t_1$  to flow from A to B is noted with a stopwatch. Then the apparatus is cleaned and the experiment is repeated with water taking about the same volume. The time of flow of water  $t_2$  from A to B is recorded. The density of the liquid  $d$  and that of water  $d_w$  are determined with the help of density bottle. The relative viscosity is calculated from the expression

$$\eta/\eta_w = dt_1/d_w t_2$$

where  $\eta$  is coefficient of viscosity of the experimental liquid and  $\eta_w$  is the coefficient of viscosity of water. Knowing the value of coefficient of viscosity of water  $\eta_w$  at the temperature of experiment, the absolute viscosity coefficient  $\eta$  of the given liquid can be found.

### 4.5.3.3 Viscosity and chemical constitution

As you know viscosity is largely due to intermolecular attractions which resist the flow of liquid. Therefore some sort of relationship between viscosity and molecular structure should be there. Viscosity is also dependent on the shape, size and mass of the liquid molecules. The following general rules have been discovered.

(i) **Dunstan Rule:**

Dunstan in 1909 showed that coefficient of viscosity  $\eta$  and molecular volume (d/M) were related as  $d/M \times \eta \times 10^6 = 40$  to  $60$

This expression holds only for normal (unassociated) liquids for associated liquids the value is much higher than 60. For example the value for benzene is 73 and for water it is 559 and for ethanol it is 189. This shows benzene is a normal liquid while water and ethanol are associated liquids.

(ii) **Molar Viscosity:**

The product of molar surface and viscosity is termed as molar viscosity. That is  
molar viscosity = molar surface  $\times$  viscosity

$$= (M/d)^{2/3} \times \eta$$

Thorpe and Rodger (1894) found that molar viscosity is an additive property at the boiling point. They worked out the molar viscosity contributions of several atoms (C, H, O, S, etc) and groups. From these, they calculated the molar viscosity of liquid from its proposed structure. By tallying this value with the experimental one, they were able to ascertain the structure.

(iii) **Rheochor:**

Newton Friend (1943) showed that if molecular volume (M/d) be multiplied by the eighth root of the coefficient of viscosity it gives a constant value [R], it is termed as Rheochor

$$M/d \times \eta^{1/8} = R$$

Like parachor, rheochor is both additive and constitutive property.

## 4.6 REFRACTIVE INDEX

### 4.6.1 Definition

When a ray of light passes from air into denser medium say a liquid, it is bent or refracted towards the normal. The ratio of the sine of angle of incidence and the sine of angle of refraction is constant and characteristic of that liquid. This is known as Snell's law. **The constant ratio n is called refractive index of the liquid** and may be written as

$$\sin i / \sin r = n$$

The ratio of sines of the angles of incidence and refraction is identical with the ratio of the velocity of light in two media.

$$\text{Thus } n = \sin i / \sin r = \frac{\text{velocity in air}}{\text{velocity in liquid}}$$

when a ray of light passes from a rarer to denser medium it can be shown from law of refraction that

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

$n_1$  is refractive index of rarer medium

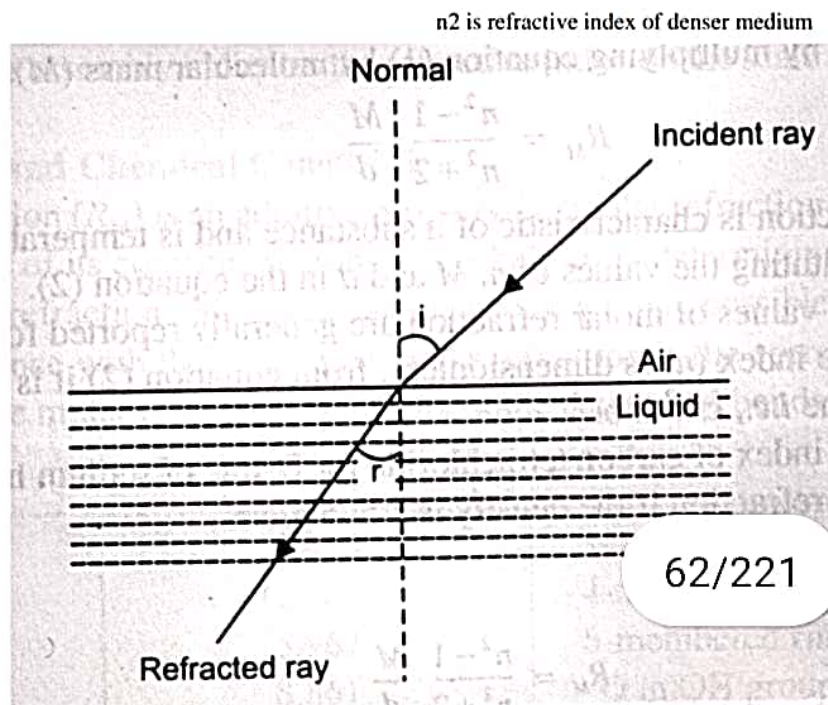


Fig 4.15

### 4.6.2 Determination of refractive index

The instruments used for determining refractive index are known as refractometers.

#### Pulfrich-refractometer:

This refractometer is very accurate and simple in principle. It is indicated diagrammatically in fig 4.16. The main part of the instrument

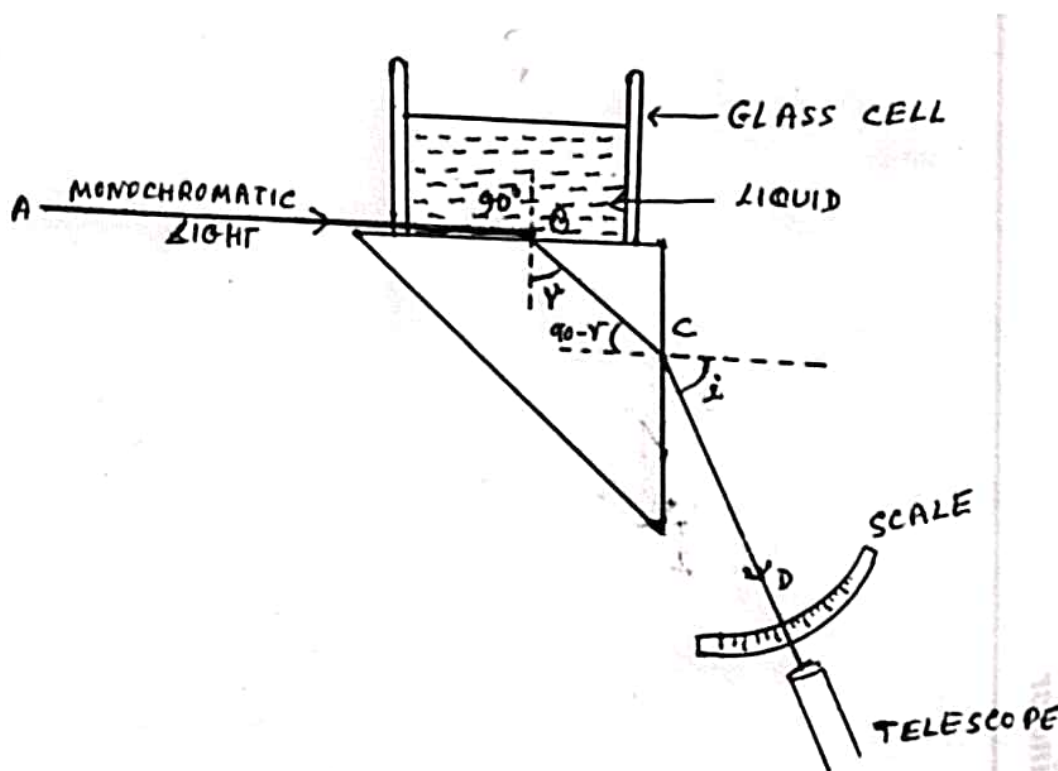


Fig 4.16 The optical system of Pulfrich refractometer

is a right angled glass prism with a small glass cell connected to its top. The liquid under examination is placed in the cell and a beam of monochromatic light is made to enter the liquid at an angle of  $90^\circ$  along the surface between the liquid and the prism. If the telescope is moved to make an angle with the horizontal which is less than  $i$  no light can reach it. At this angle  $i$  a sharp boundary between a dark and a bright field can be seen through the telescope.

For a ray of light passing from the liquid into the prism, if  $r$  be the angle of refraction when the angle of incidence is  $90^\circ$  we have already stated that  $\sin r = n_1 / n_2$  .....(1)

Where  $n_1$  is the refractive index of the liquid and  $n_2$  is that of glass prism. It is also clear to you from the fig 4.16 that

$$\sin i / \sin (90-r) = n_2 \quad \text{.....(2)}$$

$$\text{or } \sin i / \cos r = n_2 \quad \text{.....(3)}$$

$$\text{or } \cos r = \sin i / n_2 \quad \text{.....(4)}$$

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

substituting the value of  $\cos r$  in equation (4)

we get

$$\sin r = \sqrt{(1-\sin^2 i / n_2^2)} \quad \text{.....(5)}$$

From equation (1) we get

$$\begin{aligned} n_1 &= n_2 \sin r \\ &= \sqrt{n_2^2 - \sin^2 i} \end{aligned}$$

If the refractive index  $n_2$  of the glass is known and angle  $i$  is measured  $n_1$  the refractive index  $n_1$  of liquid can be calculated.

### 4.6.3 Refractive index and chemical constitution

Lorenz and Lozentz (1880) purely from theoretical considerations derived the following relation for refracting power of substance

$$R = \frac{n^2-1}{n^2+2} \times \frac{1}{d} \quad \text{.....(1)}$$

where  $R$  is specific refraction,  $d$  the density and  $n$  the refractive index. The value of  $R$  was constant at all temperatures.

#### Molar refraction:

It is defined as the product of specific refraction and molecular mass. Thus molar refraction is obtained by multiplying equation (1) by molecular mass ( $M$ ).

$$R_M = \frac{n^2-1}{n^2+2} \times \frac{M}{d} \quad \text{.....(2)}$$

The value of molar refraction is characteristic of a substance and is independent of temperature. Since it depends on wavelength of light, the values of molar refraction are generally reported for D-line of sodium.

Molar refraction  $R_M$  is an additive and constitutive property. The molar refraction of a molecule is thus a sum of the contributions of the atoms (atomic refraction) and bonds (bond refraction). From the observed value of  $R_M$  of appropriate known compounds, the atomic refractions of different elements and bonds have been worked out.



## 4.7 LIQUID CRYSTALS

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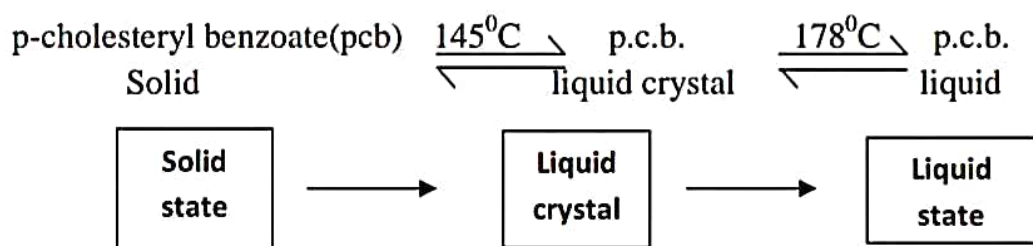
### 4.7.1 Definition

There are certain solids which on heating undergo two sharp phase changes one after the other. They first fuse sharply yielding turbid liquids and again equally sharply at higher temperature yielding clear liquids. These changes get reversed on cooling at the same temperature. The turbid liquid show anisotropy i.e. they have different physical properties from different directions. Anisotropy is particularly seen in the optical behaviour of liquids. In an anisotropic substance, the physical property are different in different direction. On the other hand true liquids are isotropic ie same physical properties in different directions. As anisotropic properties are associated with crystalline state, the turbid liquids are known as liquid crystals.

This liquid crystal term, however, is not satisfactory since the substances in this state do not have properties of crystalline state. Actually, they are more like liquids in having properties like mobility, surface tension, viscosity etc. Amongst other names that have been suggested are crystalline liquids and anisotropic liquids, but these are also not satisfactory. The term mesomorphic state (meaning intermediate form) probably fits best. But, the older term liquid crystal continues to be used even in the present day literature.

Substances which show the above behaviour are usually some long chain organic molecules either terminating in groups such as-OR, -COOR or having groups like  $-C=N-$ ,  $-N=NO-$ ,  $-C=C-$  in the middle. The first solid showing this peculiar property was discovered in 1888 was cholesteryl benzoate  $C_6H_5COOC_{27}H_{45}$ . It fuses sharply at  $145^{\circ}C$  to form turbid liquid and on further heating changes into clear liquid at  $178^{\circ}C$ . If we cool, the above changes are reversed i.e., the clear liquid when cooled first changes into turbid state at  $178^{\circ}C$  and then into the solid state at  $145^{\circ}C$

Later on, p-azoxyanisole and p-azoxyphenetone were found to exhibit the same properties. In 1991 P.G. De Genees, a French physicist got the Nobel Prize in Physics for contribution to liquid crystals and polymers.



One such substance that forms liquid crystal is p-ozoxyanisole (Fig 4.17)

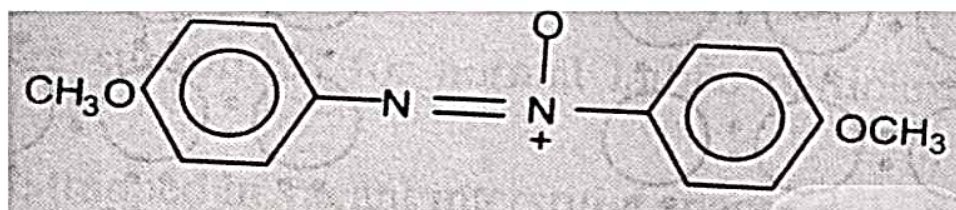


Fig 4.17 p-Ozoxyanisole

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## 4.8 STRUCTURE OF LIQUID CRYSTALS

In a liquid the molecules have random arrangement and they are able to move past each other. In a solid crystal the molecules have an ordered arrangement and are in fixed positions. In a liquid crystal, however, molecules are arranged parallel to each other and can flow like a liquid. **Thus liquid crystals have the fluidity of a liquid and optical properties of solid crystals.**

Accordingly to their molecular arrangement, the liquid crystals are classified into three types

(i) **Nematic liquid crystals:**

in nematic liquid crystals molecules are parallel to each other like soda straws but they are free to slide or roll individually.

(ii) **Smectic liquid crystals:**

The molecules in this type of liquid crystals are also parallel but these are arranged in layers. These layers can slide past each other (Fig 4.18).

(iii) **Cholesteric liquid crystals:**

As in nematic crystals in this type liquid crystals the molecules are parallel but arranged in layers. The molecules in successive layers are slightly rotated with respect to the layers above and below so as to form spiral structure.

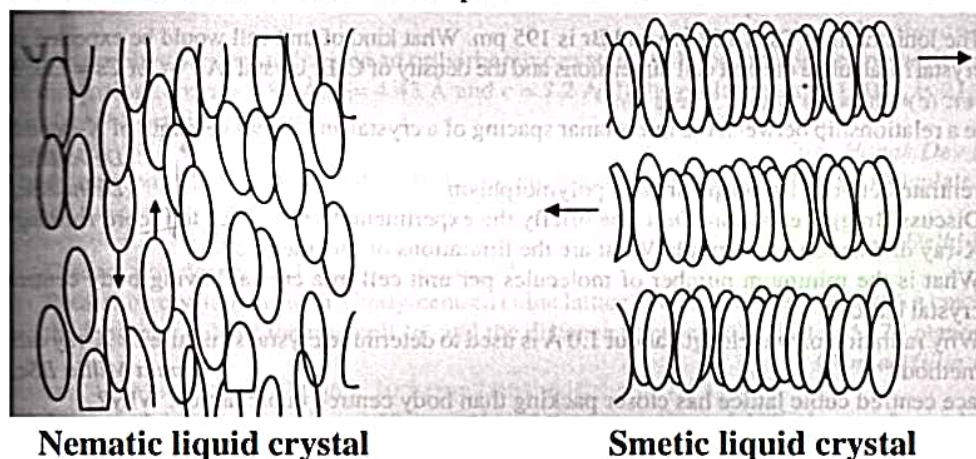


Fig 4.18

**Application of liquid crystals:**

On account of their remarkable optical and electrical properties, liquid crystal found several practical applications. Some of these are given below.

**Number display:**

When a thin layer of nematic liquid crystal is placed between two electrodes and an electrical field is applied, the polar molecules are pulled out of alignment. This cause the crystal to be opaque. Transparency returns when electrical signal is removed. This property is used in the number displays of digital watches, calculators, and other instruments.

**Monitoring body temperature:**

Like the solid crystals, liquid crystals can diffract light. Only one of the wavelengths of the white light is refracted by the crystal which appears coloured. As the temperature changes the distance between the layers of molecules also changes. Therefore the colours of the reflected light changes correspondingly. These colesteric liquid crystal undergoes a series of colour changes with temperature. These crystals are used in indicator tapes to monitor body temperature or to spot areas of overheating in mechanical systems.

**4.9 SUMMARY**

In this unit you have studied liquid state in detail. Various properties of liquids such as vapour pressure, surface tension, viscosity and refractive index have been discussed and also their usefulness to elucidating molecular structure.

The difference between liquid, liquid crystal and solid state have been discussed and also liquid crystal in detail.

Thought the study of the parachor, molecular viscosity, molar refraction etc. Are useful in elucidating molecular structure of compounds, but they give some rough idea about molecular structure. Mass Spectra, I.R., NMR are the latest methods/techniques for elucidating molecular structure of organic compounds accurately.

**4.10 TERMINAL QUESTIONS****(A) Multiple Choice Questions:**

1. The reciprocal of viscosity is known as:

- (a) Anti viscosity                      (b) intrinsic viscosity  
(c) Reduced viscosity (d) Fluidity

Ans (d)

2. The molecules which have partial positive charge at one end and partial negative charge at the other are called:

- (a) ion pairs                              (b) charged molecules  
(c) dipole                                  (d) electric molecule

Ans (c)

3. With the rise of temperature the surface tension of a liquid:

- (a) Increases                              (b) decreases  
(c) remains the same (d) none of the above

Ans (b)

4. The unit in which surface tension is measured is:

- (a) dyne cm                                      (b) dyne cm<sup>-1</sup>  
 (c) dyne<sup>-1</sup> cm                                    (d) dyne<sup>-1</sup> cm<sup>-1</sup>

Ans (b)

5. Which of the following liquids has maximum viscosity:

- (a) water                                      (b) ethyl alcohol  
 (c) Acetone                                    (d) glycerine

Ans (d)

6. Small droplets are spherical in shape. It is due to:

- (a) High viscosity  
 (b) their tendency to acquire minimum surface area  
 (c) Less viscosity  
 (d) their tendency to acquire maximum surface area

Ans (b)

**(B) Short Answer Questions:**

- Define surface tension. What is its unit?
- How does vapour pressure varies with temperature.
- Explain why
  - Drops of liquids are spherical in shape.
  - At the boiling point, the temperature of liquid does not rise although it is being heated.
  - Glycerol is more viscous than water.
- Write a note on specific refraction.
- Write a note on liquid crystals.
- Explain the term viscosity of a liquid.

**(C) Long Answer Questions:**

- Define the terms surface tension and surface energy. Discuss capillary rise method for determination of surface tension in the laboratory.
- What are liquid crystals? How are they classified? How would you account for turbidity observed in liquid crystals? What are the uses of liquid crystals?
- Why do you use the same viscometer for the liquid and water during the experimental determination of the viscosity of the liquid by Ostwald viscometer? Describe the experiment.
- Write a note on parachor. How parachor is useful in elucidating molecular structure of compounds at 20<sup>0</sup>C toluene rises 1.95 cm in the capillary tube of radius of 0.3412 mm. Calculate the surface tension of toluene. The density of toluene at 20<sup>0</sup>C is 0.866 cc

Hint : use the formula  $\gamma = \frac{hrdg}{2}$  dynes/cm

- (a) Define viscosity of a liquid. What is the effect of temperature on viscosity?

- (c) Water passes through a viscometer in 30 seconds and ethanol in 175 seconds at 20°C. If the density of water is 0.998g/cm<sup>3</sup>, density of ethanol is 0.790g/cm<sup>3</sup> and viscosity of water is 0.01008 poise, calculate the viscosity of ethanol.

(Hint : use formula  $\eta = \eta_w dt_1/dwt_2$

ans 0.01747 poise)

6. Write notes on the following

- (a) Vapour pressure
- (b) Optical oxaltation
- (c) Ramsay- Shields equation

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