LIQUIDS

2.1.0 INTRODUCTION

Matter exists in three states i.e., gases, liquids and solids. The chapter of the liquids is mostly concerned with the discussion of the important physical properties like vapour pressure, viscosity, surface tension, refractive index and dipole moment and magnetic properties etc. The importance of these physical measurements has considerably increased during the recent years. These properties are useful to know the composition and structure of the molecules of liquids especially.

2.1.1 Types of properties:

The properties based upon the certain measurements are of four types.

(a) Additive Properties:

Those properties which are concerned with individual atoms. These properties do not change, no matter in which physical or chemical state they exist. Mass and weight of an atom do not change and we can find out the molar mass of a substance by simply adding of the atomic weights present in the molecule. Molecular heat of a compound is the sum of atomic heats of the atoms present in it. Radioactivity is the property of individual atoms and it is also an additive property.

(b) Constitutive Properties:

Those properties which entirely depend upon the arrangement of atoms in a molecule are called constitutive properties. They do not depend upon their number. So, vapour pressure, viscosity, surface tension, dipole moment, refractive index and optical activity are constitutive properties.

(c) Additive and Constitutive Properties:

These are additive properties, but their additive character is modified by the manner in which the atoms are linked together. Parachor, rheochor, polarization are both additive and constitutive properties.

(d) Colligative Properties:

Those properties which depend upon the number of particles, but not upon their nature and structure are called colligative properties. There are four colligative properties of solutions and they depend upon the number of particles of solutes. These properties are,

(i)   Lowering of vapour pressure

(ii) Elevation of boiling point   (Ebullioscopy)

(iii) Depression of freezing point (Cryoscopy)

(iv) Osmotic pressure

2.1.2 Properties of liquids:

Now we are going to discuss a few properties of liquids as surface tension, viscosity, refractive index, dipole moment, polarizability and magnetic properties.

2.2.0 SURFACE TENSION

The molecules of a liquid at its surface feel different forces of attractions than those molecules, which are in the interior of the liquid. A molecule lying inside the liquid is surrounded by other molecules and is attracted in all the directions. The net force of attraction is zero. The molecule lying at the surface experiences a net inward attraction. So, the surface behaves as if it is under tension. This property of liquid is called surface tension. Following diagram (1) makes the idea clear.
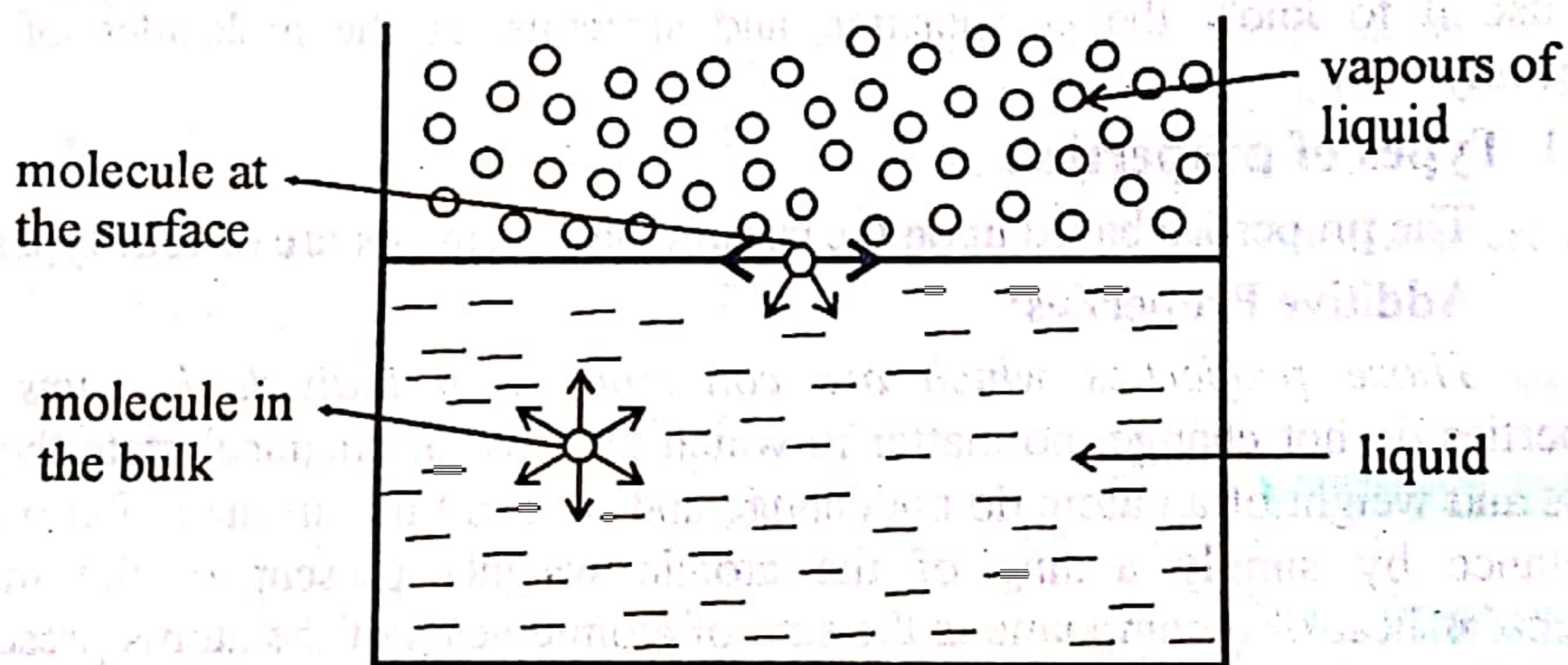

Fig. (1). The attractive forces which are experienced by the molecules at the surface and inside the molecules.

Definition: Surface tension is defined in two ways.

(i)   "It is the work in joules required to produce a unit increase in surface area. So, it is expressed in $J\,m^{-2}$." The old unit is $erg\,cm^{-2}$.

(ii) "It is the force in Newtons acting along the surface of the liquid at right angles to any line one meter in length." Its units are $N\,m^{-1}$. The old units of surface tension is $dynes\,cm^{-1}$.

2.2.1 Surface Energy:

In order to understand the surface energy, take into consideration the first definition of surface tension. When we increase the surface area of liquid, some work has to be done against the inward pull. For that purpose, consider a soap solution film contained in rectangular wire form A, B, C, D, in which the side AB is moveable Fig. (2).
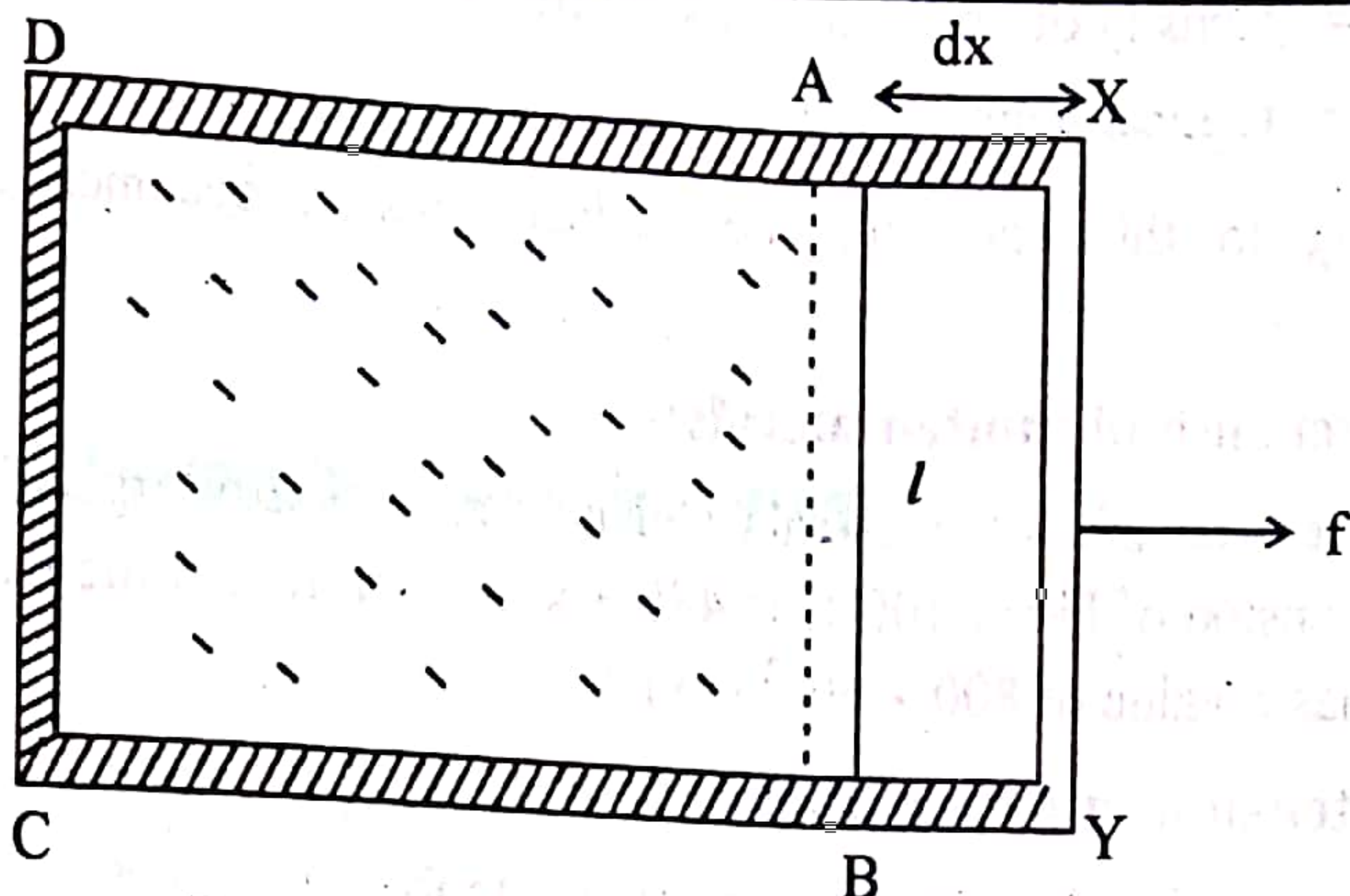
Fig. (2) Force of surface tension of a liquid.

In order to extend the surface area of the film the moveable wire has to be pulled to position XY. For this change, work has to be done against the surface tension,

$$\text{work} = \text{force} \times \text{distance} = f \times dx = (\gamma 2l)dx$$
$$\text{work} = \gamma \, 2l \, dx = \gamma \, 2dA \qquad (\because \, l \, dx = dA)$$

where 'γ' is constant of proportionality and is called surface tension.

2.2.2 Effect of Temperature on Surface Tension:

The surface tension of a liquid decreases as the temperature increases. At high temperatures, the intermolecular forces decrease and hence the tension on the surface becomes less. Following table (1) shows the surface tension of certain liquids in N m^{-1} at various temperatures.

Table (1). Surface tension of liquids at different temperatures
(N m^{-1} × 10^{+3} = milli N m^{-1}) (1 milli Nm^{-1} = 1 dyne cm^{-1})

Temp (°C)	H$_2$O	C$_2$H$_5$OH	C$_6$H$_5$ – NO$_2$	CCl$_4$	C$_6$H$_6$
0	75.67	24.00	46.30	28.90	31.60
25	71.98	21.90	43.30	26.10	28.20
50	69.89	19.80	40.10	23.10	25.20
75	63.45	—	37.50	20.20	21.89

(In order to get the values in Nm^{-2}, divide above values by 1000 = 10^{+3})

The comparison shows that surface tension of H$_2$O has greater values than other liquids at various temperatures.

The important relationship between temperature and surface tension is as following.

$$\gamma \times \left(\frac{M}{D}\right)^{2/3} = k \, (T_C - T) \qquad \dots\dots (1)$$

γ = Surface tension of liquid at a temperature 'T'.

M = Molar mass of the liquid.

D = Density of liquid at temperature 'T'.

T_C = Critical temperature of the liquid.

According to this equation, the surface tension becomes zero, when $T = T_C$.

2.2.3 Surface tension of molten metals:

Surface tension of molten metals and molten salts are larger than organic liquids. Surface tension of Hg at 100°C is 480.3×10^{-3} N m^{-1}, while that of molten silver at 800°C has a value of 800×10^{-3} N m^{-1}.

2.2.4 Surface tension in a daily life:

Phenomenon of surface tension is responsible for

(i)   Formation of globules.

(ii)   Formation of rain drops.

(iii) Rise of water in the capillary tubes.

(iv)   Movement of liquids in the porous materials like blotting paper and soil.

(v)   Rise of water from the roots to the top of the trees.

2.2.5 Reasons for the rise of liquids in the capillary tube:

Those liquids which wet the solid surfaces rise in the capillary tubes. This rise is due to inward pull of the surface which pushes the liquid into the capillary tube. Following diagram (3) shows that how the liquid is compelled to enter the capillary tube from the lower side.
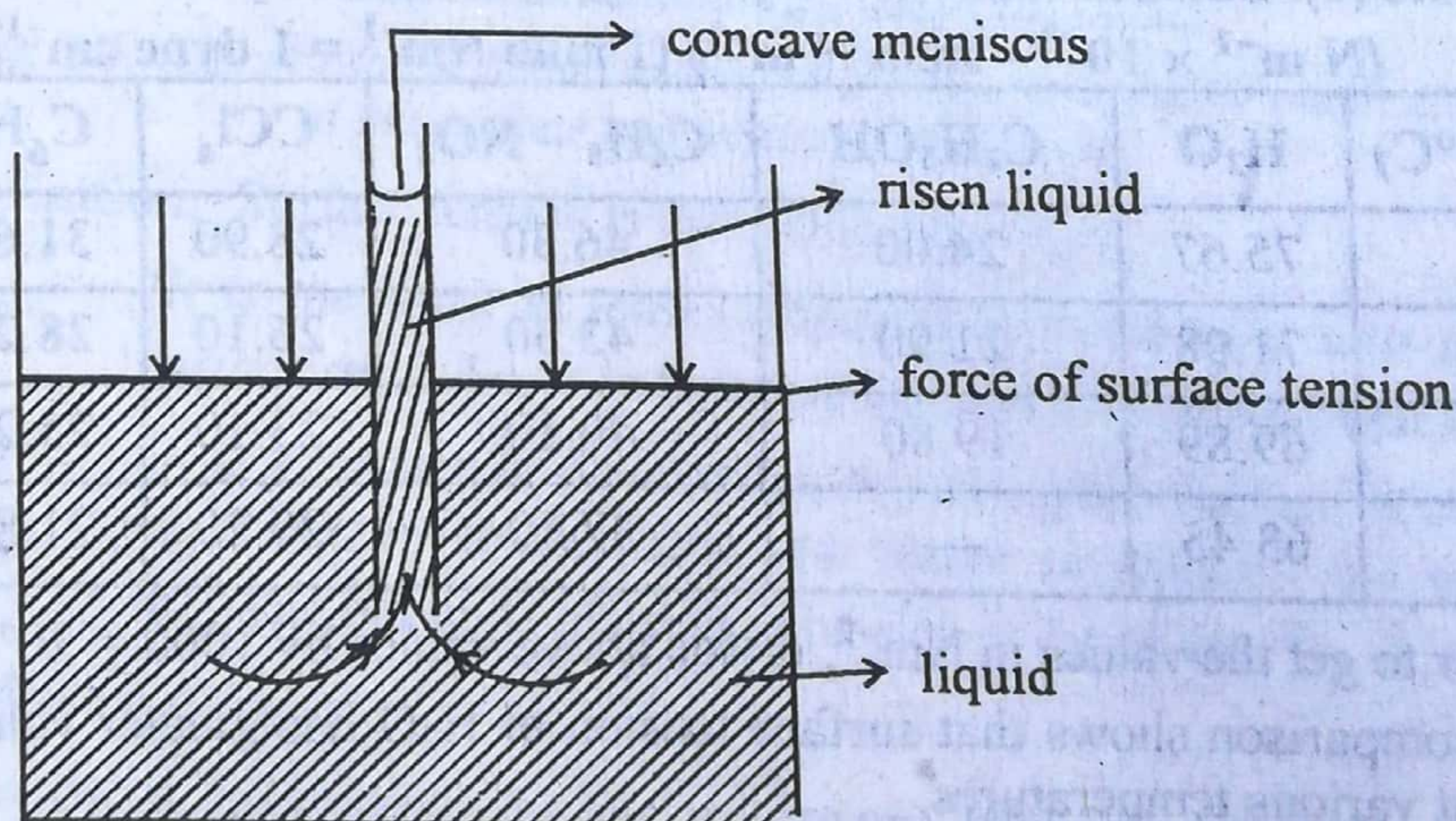

Fig. (3) How the liquid is compelled to rise in the capillary tube.

In the case of wetting liquids, the adhesive forces are greater than the cohesive forces. Adhesive forces are present among the molecules of the liquids and the solid surface of the capillary tube. Cohesive forces are present among the molecules of liquids.

2.2.6 Contact angle:

When the liquid rises in the capillary tube, it makes the concave meniscus upwards as shown in the diagram.

This type of meniscus is formed by the wetting liquids. The liquid is higher in level along the circumference of the capillary tube and is depressed in the center of the tube. The contact angle (θ) is inside the liquid between the solid. The solid-liquid interface as shown in the following diagram (4). The contact angle is less than 90°.
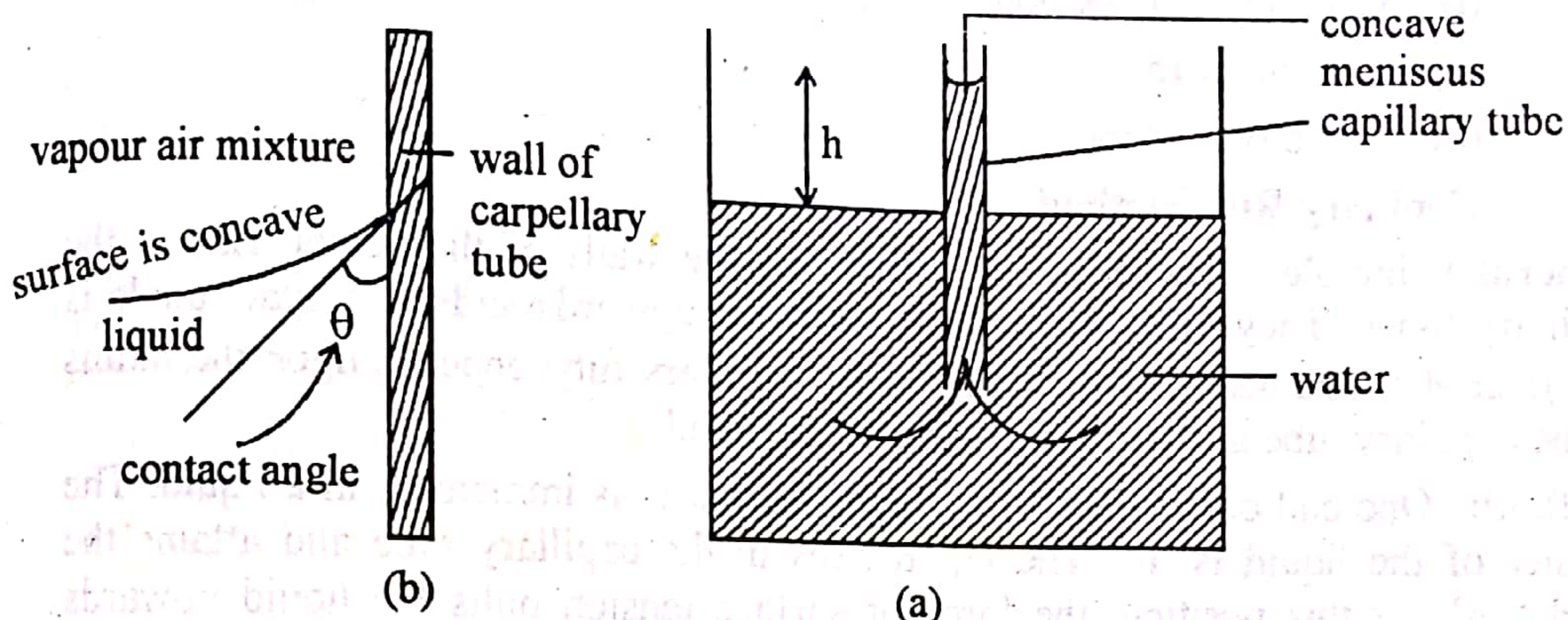

Fig. (4) Formation of concave meniscus for a rising liquids like water.

Those liquids which are depressed in the capillary tube make the convex meniscus upwards. Their contact angles are greater than 90° as shown in the following diagram (5).
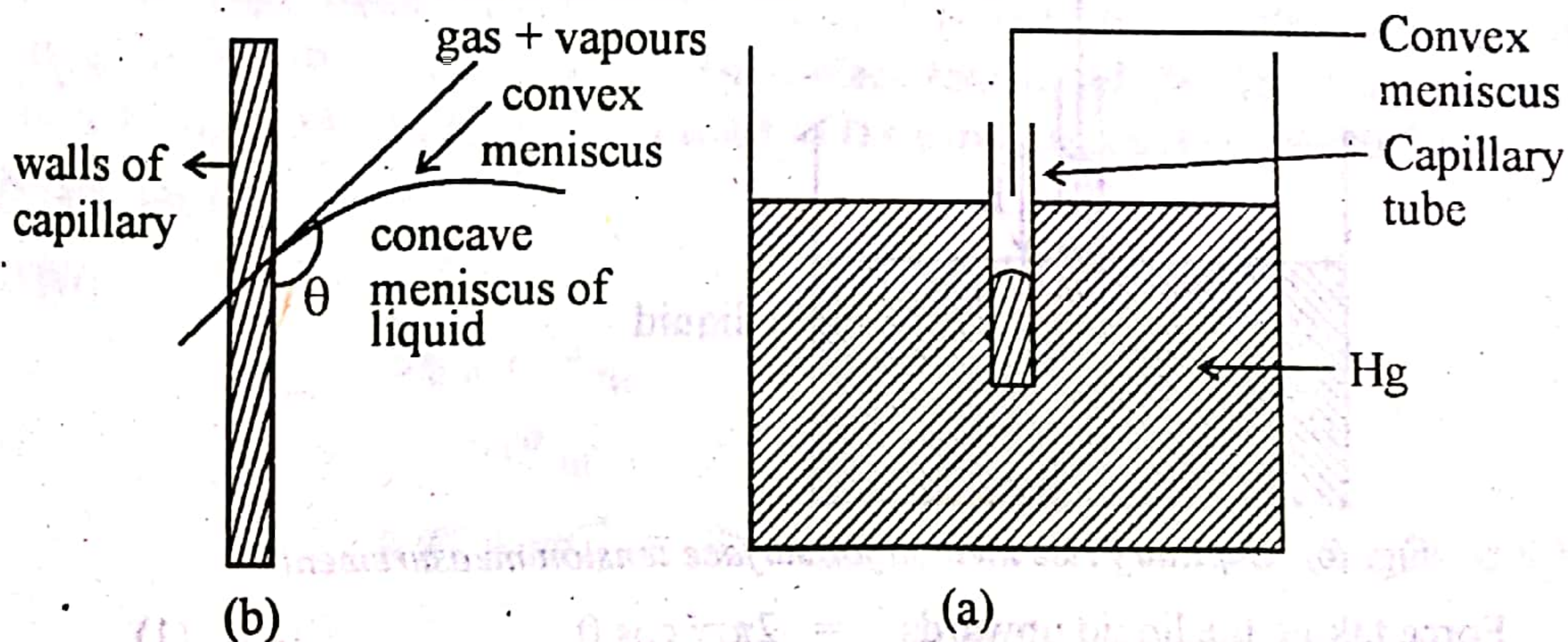

Fig. (5) Formation of convex meniscus for a falling liquids like mercury.

2.2.7 Interfacial tension:

Take two immiscible or partially miscible liquids in a vessel. A force of surface tension is acting along their surface of separation. This is called interfacial tension. Its value is generally intermediate between the surface tension of two liquids. But sometimes, it is less than both. The reason for this is that at the interface the molecules of a liquid are attracted by the molecules of the other.

2.2.8 Surface Active Agents:

"Those substances which lower the surface tension of water are called surface active agents." Substance like soaps, detergents, methyl alcohol, ethyl alcohol and acetone decrease the surface tension of water.

If a greasy spot is present on the surface of a cloth, then water can not wet the cloth at that place due to its high surface tension. So grease can not be removed by water alone. When soap is added to water, it lowers the interfacial tension between water and grease. The grease mixes up into soap solution, so grease is removed from the surface of cloth.

2.2.9 Measurement of Surface Tension:

Some important methods, for the measurement of surface tension are as follows.

(i)   Capillary rise method

(ii) Torsion method

(iii) The drop method

(i)   Capillary Rise Method:

General Principle: Those liquids which wet the walls of the vessel, rise in the capillary tubes. They form the concave meniscus upwards and the contact angle is less than 90°. The height of the liquid in the capillary tube depends upon the radius of the capillary tube and surface tension of the liquid.

Method: One end of the capillary tube of radius 'r' is immersed in a liquid. The density of the liquid is 'd'. The liquid rises in the capillary tube and attains the height 'h'. At this position, the force of surface tension pulls the liquid upwards and it is counterbalanced by the downward gravitational pull. The force which is acting upwards is calculated in terms of radius of the capillary tube 'r', surface tension 'γ' and contact angle 'θ'. Following diagram (6) makes the idea clear.
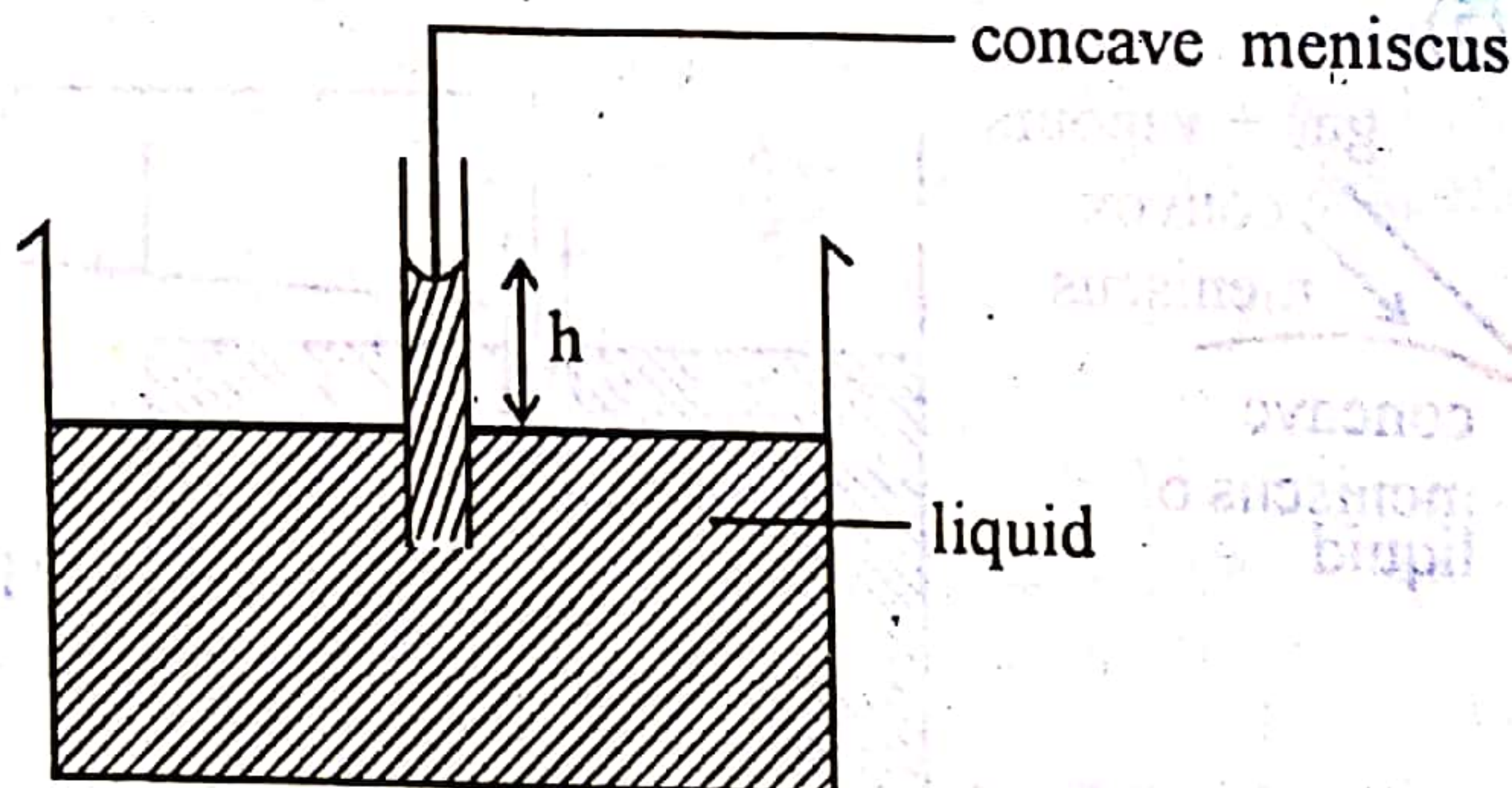

Fig. (6) Capillary rise method for surface tension measurement.

Force taking the liquid upwards $= 2\pi r \gamma \cos \theta$ ...... (1)

$$\gamma = \text{surface tension of liquid}$$
$$r = \text{radius of capillary tube}$$
$$2\pi r = \text{diameter of capillary tube}$$

Downward force is the weight of the liquid. In order to calculate the weight of the liquid, we proceed as follows,

Radius of capillary tube $= r$

Base area of tube $= \pi r^2$

Height of liquid $= h$

Volume of liquid risen in the capillary tube $= \pi r^2 h$

Density of liquid $= d$

Since, mass of a substance $=$ volume $\times$ density

So,

Mass of liquid risen in the capillary tube $= \pi r^2 h \times d$

Weight of liquid risen in capillary tube $= \pi r^2 h \, d \, g$ ...... (2)

These two forces given by equation (1) and (2) are balanced,

$$2 \pi \, r \, \gamma \cos \theta = \pi r^2 h \, d \, g$$

$$\gamma = \frac{r \, h \, d \, g}{2 \cos \theta} \quad \text{...... (3)}$$

If the radius of the capillary tube is very small, then the contact angle 'θ' approaches to zero.

$$\cos (0°) = 1$$

$$\gamma = \frac{r \, h \, d \, g}{2} \quad \text{...... (4)}$$

So, if we want to calculate the value of 'γ' we need the values of r, h, d and g. The capillary tube must be of very small diameter.

EXAMPLE (1)

A liquid whose density is 0.85 g cm^{-3} rises in the capillary tube up to a height of 5×10^{-2} m. Calculate the surface tension of the liquid assuming the contact angle θ to be zero. The radius of the capillary tube is 0.9×10^{-4} m.

SOLUTION:

Data:

$$r = 0.9 \times 10^{-4} \text{ m}$$

$$h = 5 \times 10^{-2} \text{ m}$$

$$d = 0.85 \text{ g cm}^{-3} = 850 \text{ kg m}^{-3} \text{ (The units of r, h, d should be S.I.)}$$

$$g = 9.80 \text{ ms}^{-2}$$

Since

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

Putting the values of all parameters in S.I. units

$$\gamma = \frac{1}{2} (0.9 \times 10^{-4} \text{ m}) (5 \times 10^{-2} \text{ m}) (850 \text{ kg m}^{-3}) \times (9.8 \text{ ms}^{-2})$$

$$\gamma = 18742.5 \times 10^{-6} \text{ Nm}^{-1} = \boxed{1.87 \times 10^{-2} \text{ Nm}^{-1}} \quad \text{Ans.}$$

(ii)   Torsion Method:

General principle:

In this method, the surface tension is measured by measuring the force required to detach a horizontal platinum ring from the surface of the liquid. Greater the surface tension of liquid, greater the force required to pull up the ring.

Method:

This method is based upon torsion balance after the name of du-Nouy. As shown in the following diagram (7), the platinum ring of radius 'r' suspended by a hook on the beam. A screw 'S' is used to fix the pointer 'P'. 'T' is the torsion wire. This wire is so adjusted that the beam 'A' is in horizontal position. Liquid is placed in the dish 'B'. The height of the dish 'B' is controlled by the screw 'S'. It is adjusted in such a way that, liquid just touches the ring. The knob 'C' is turned slowly till the ring is detached from the surface of the liquid. During this process the reading on the circular scale 'D' is kept in its horizontal position by means of screw 'S'.

Following equation is used to calculate the surface tension of liquid.

$$\gamma = \frac{Mg}{4\pi r}$$

M = mass of liquid film in the ring
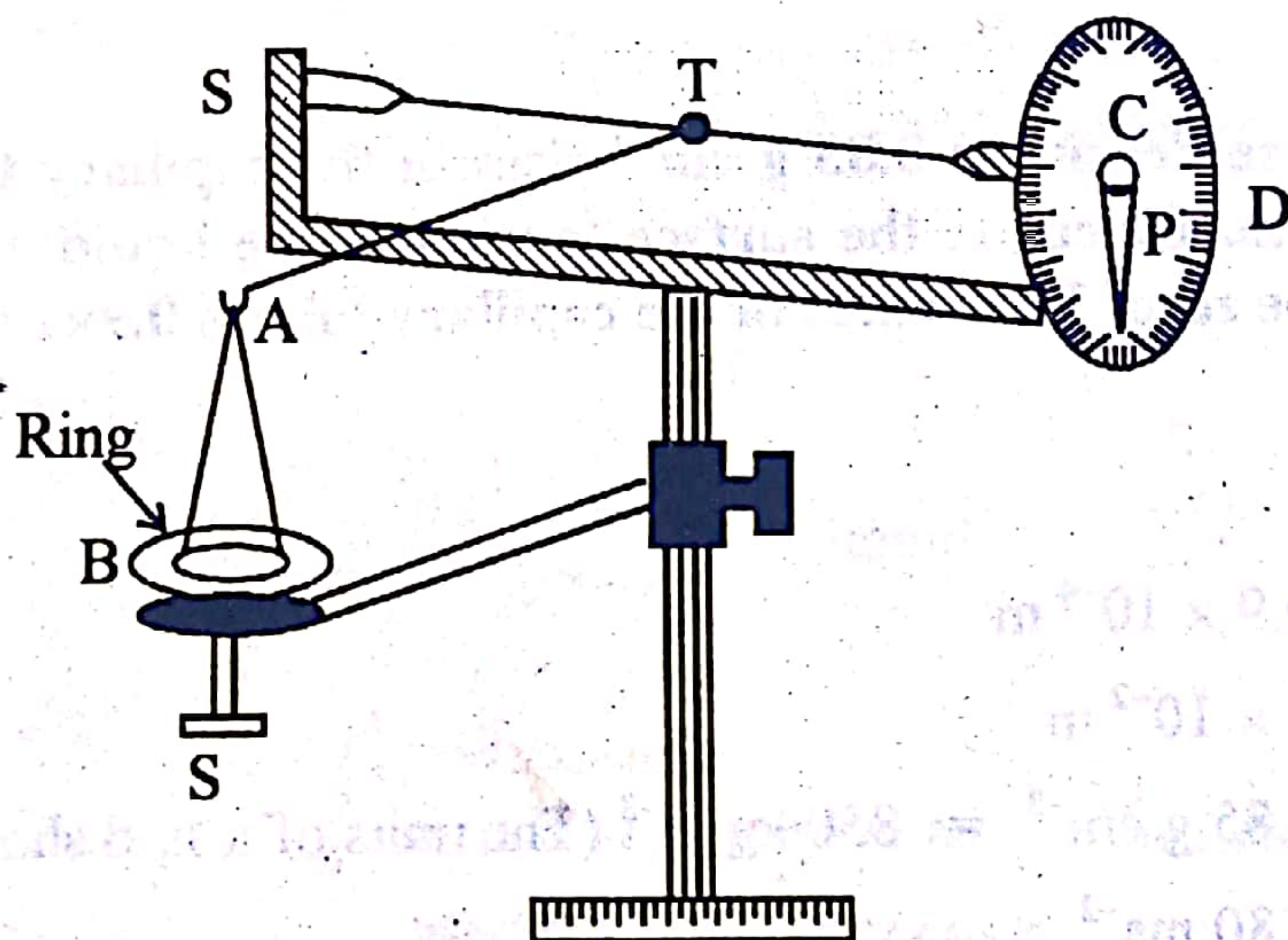
r = radius of platinum ring

Fig. (7) du-Nouy's torsion balance for measuring surface tension.

(iii)   Drop Method:

General Principle:

When the liquid falls under the force of gravity, it forms the drops. The drop is supported by the upward force of surface tension acting at the outer circumference of the drop. The weight of the drop pulls it downward. When these two forces are balanced, then the calculations are done.

There are two ways to do the calculations.

(i)   Measurement of the weight of the drops.

(ii)   Counting of the number of drops.

Drops weight method:

The apparatus used for this purpose is a glass pipette, with a capillary at the lower end. This apparatus is called stalagmometer or drop pipette, as shown in the following diagram (8).
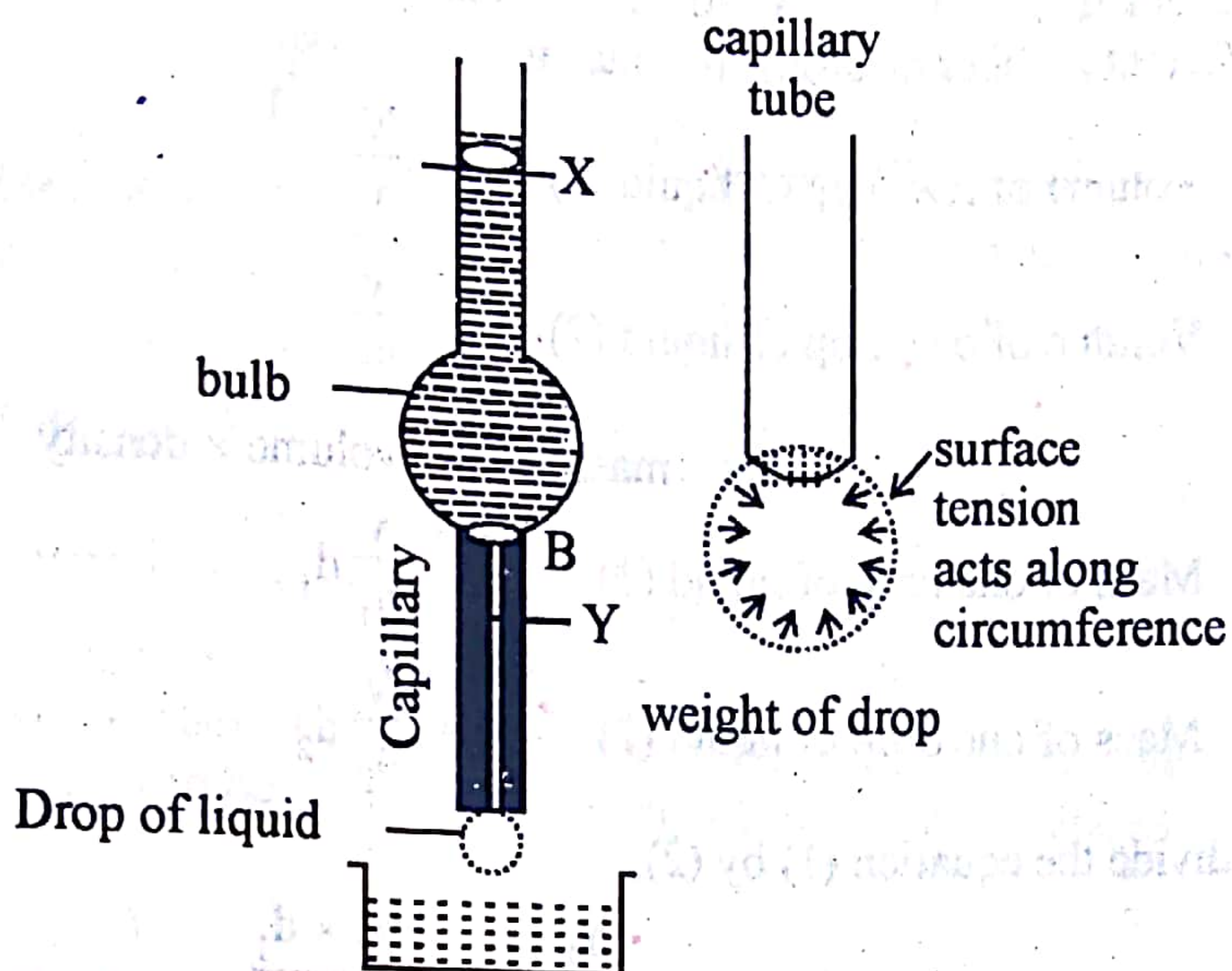

Fig. (8) Stalagmometer to measure the surface tension of a liquid.

Around twenty drops of the given liquid are received from the drop pipette in a weighing bottle. In this way, the weight of one drop in calculated. Then the stalagmometer is cleaned and dried and filled with a reference liquid say water and weight of one drop of water is calculated in the similar manner.

Since, for any drop,

$$mg = 2\pi r \gamma \qquad \cdots\cdots (1)$$

m = mass of the drop.

r = radius of the tube

γ = surface tension.

When we apply this equation on two liquids, then

$$m_1 g = 2\pi r \gamma_1 \qquad \cdots\cdots (2)$$

$$m_2 g = 2\pi r \gamma_2 \qquad \cdots\cdots (3)$$

Dividing equation (2) by (3)

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} \qquad \cdots\cdots (4)$$

When we know the surface tension of the reference liquid i.e., water, then that of other can be calculated, because we know the masses of drops.

(iv)   Drop number method:

The stalagmometer is filled up to the mark 'X' with the liquid, whose surface tension is to be measured. The number of drops are counted till the liquid flows up to the mark 'Y'. Similarly, the number of drops of the reference liquid say water are counted from mark 'X' to 'Y'. Volume of the both liquids is same say 'V' with different number of drops 'n_1' and 'n_2'.

$$\text{Volume of one drop of liquid (1)} = \frac{V}{n_1}$$

$$\text{Volume of one drop of liquid (2)} = \frac{V}{n_2}$$

Since,   mass   =   volume × density

$$\text{Mass of one drop of liquid (1)} = \frac{V}{n_1} d_1 \qquad \cdots\cdots (1)$$

$$\text{Mass of one drop of liquid (2)} = \frac{V}{n_2} d_2 \qquad \cdots\cdots (2)$$

Let us divide the equation (1) by (2),

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2 \times d_1}{n_1 \times d_2} \qquad \cdots\cdots (3)$$

The density of the liquid under test is measured by the specific gravity bottle. The values of 'd_2' and 'γ_2' for the reference liquid say water can be consulted from the literature.

EXAMPLE (2)

The number of drops of an unknown liquid and water are 86 and 29 respectively at 25°C in a stalagmometer. The surface tension of water is 7.2 × 10^{-2} Nm^{-1} and density of liquid is 0.8 g cm^{-3}. Calculate the surface tension of liquid.

SOLUTION:

Data:

$$n_l = 86$$
$$n_w = 29$$
$$d_l = 0.8 \text{ g cm}^{-3} = 8 \times 10^2 \text{ kg m}^{-3}$$

(because we need S.I. units of density)

$$d_\omega = 1 \times 10^3 \text{ kg m}^{-3}$$
$$\gamma_w = 7.2 \times 10^{-2} \text{ Nm}^{-1}$$
$$\gamma_l = ?$$

Formula used

$$\gamma_l = \frac{n_w \, d_l}{n_l \, d_w} \times \gamma_\omega$$

Putting values

$$\gamma_l = \frac{(29)\,(8 \times 10^2)\,(7.2 \times 10^{-2})}{(86)\,(1 \times 10^3)} \left(\frac{kg\ m^{-2}\ Nm^{-1}}{kg\ m^{-3}} \right)$$

$$= \frac{1670}{86 \times 10^{+3}}\ Nm^{-1}$$

$$\gamma_l = 19.42 \times 10^{-3} - Nm^{-1} = \boxed{1.942 \times 10^{-2}\ Nm^{-1}} \quad \text{Ans.}$$

2.3.0 THE PARACHOR

Macleod in 1923, gave the following mathematical relationship between the surface tension and the density of a liquid. His relationship is empirical.

$$\gamma = C(D - d)^4 \qquad \cdots\cdots (1)$$

where, γ = surface tension of liquid

D = density of liquid

d = density of the vapours of liquid

C = characteristic constant of the liquid.

This constant 'C' can give us a additive and constitutive property called parachor, which can be secured by rearranging the above equation (1).

$$\frac{\gamma}{C} = (D - d)^4$$

Taking 4th root on both sides

$$\left(\frac{\gamma}{C}\right)^{1/4} = (D - d)$$

Taking inverse

$$\left(\frac{C}{\gamma}\right)^{1/4} = \frac{1}{(D - d)}$$

Rearranging

$$C^{1/4} = \frac{\gamma^{1/4}}{(D - d)} \qquad \cdots\cdots (2)$$

In 1924, Sudgen obtained a relationship by multiplying equation(2) with the molar mass of the liquid. This constant obtained is called parachor.

$$M.C^{1/4} = \frac{M\,\gamma^{1/4}}{(D - d)} \qquad \cdots\cdots (3)$$

Let us put $[P] = MC^{1/4}$

$$[P] = \frac{M\,\gamma^{1/4}}{(D - d)} \qquad \cdots\cdots (4)$$

Since, the values of 'd' is very less as compared to 'D', so it can be ignored. (Since volume of vapours is 1600 times greater than that of liquid so density of vapours is 1600 times less).

$$[P] = \frac{M\,\gamma^{1/4}}{D} \qquad \cdots\cdots (5)$$

Since mass/volume is the density, so molar mass and density give molar volume

$$\frac{M}{D} = V_m \text{(molar volume of liquid)}$$

$$[P] = V_m \gamma^{1/4} \qquad\qquad \cdots\cdots (6)$$

So, *the parachor of a liquid is obtained from the surface tension and the molar volume of liquid.* If we manage the temperature of the liquid in such a way that its surface tension becomes unity, then

$$[P] = V_m (1)^{1/4} = V_m \qquad\qquad \cdots\cdots (7)$$

Hence, the parachor of a liquid is the molar volume of a liquid, when the surface tension of that liquid is unity.

Parachor is an additive and constitutive property.

Each atom of a molecule has a definite value of the parachor and total parachor value of a simple molecule is the sum of parachor values of constituting atoms. The parachor values which are associated with the atoms are called atomic parachors. Similarly, we have group parachors.

The units of parachor can be derived by putting the units of M, D and $\gamma^{\frac{1}{4}}$.

EXAMPLE (3)

The parachor values of C_2H_6 and C_3H_8 are 110.5 and 150.8 respectively. What values of parachor do you expect for hexane?

SOLUTION:

The difference of two values gives us the parachor equivalent of CH_2 group.

$$[P] \, C_2H_6 = 110.5$$
$$[P] \, C_3H_8 = 150.8$$
$$[P] \, CH_2 = [P] \, C_3H_8 - [P] \, C_2H_6$$
$$= 150.8 - 110.5 = 40.3$$

Since in C_6H_{14}, we have one C_3H_8 and three CH_2 units. So,

$$[P] \, C_6H_{14} = [P] \, C_3H_8 + 3[P] \, CH_2$$
$$= 150.8 + 3 \times 40.3 = \boxed{271.7} \quad \text{Ans.}$$

2.3.1 Parachor as a constitutive property:

The constitutive property of a substance depends upon the arrangement of atoms within the molecule. It has been found that the total parachor value of a molecule containing some multiple bonds or a closed ring not only depend upon the atomic parachors, but also on the number of multiple bonds or the number of rings. The following table (2) shows the values of atomic and structural parachors of some common atoms and multiple bonds along with the rings.

Table (2) Some Atomic and Structural Parachors.

Atom, group or linkage	Parachor values		Atom, group or linkage	Parachor values	
	Sugden	(Vogel)		Sugden	(Vogel)
Carbon	4.8	8.6	C = O	—	44.4
Hydrogen	17.1	15.7	– OH	—	30.2
Oxygen	20.0	19.8	– COOH	—	73.7
Nitrogen	12.5	—	– NO_2	—	73.8
Fluorine	25.7	—	Single covalent bond	0.0	0.0
Chlorine	54.3	55.5	Double bond	23.2	19.9
Bromine	68.0	68.8	Triple bond	46.6	40.0
Iodine	91.0	90.3	3-membered ring	17.0	12.3
Sulphur	48.2	—	4-membered ring	11.6	10.0
CH_2	39.0	40.0	5-membered ring	8.5	4.6
O–O in ester	60.0	—	6-membered ring	6.1	1.4

### 2.3.2 Applications of parachor for structure verification:

In order to verify the structure of the compound, we should determine the parachor in the laboratory by measuring the surface tension and putting the value of molar volume in the following equation given by Sudgen.

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

Theoretical parachor of the same compound is calculated with the help of above table by keeping in mind this structure which has been proposed.

(i)   Structure of benzene:

Kekule has given the structure of benzene as follows.
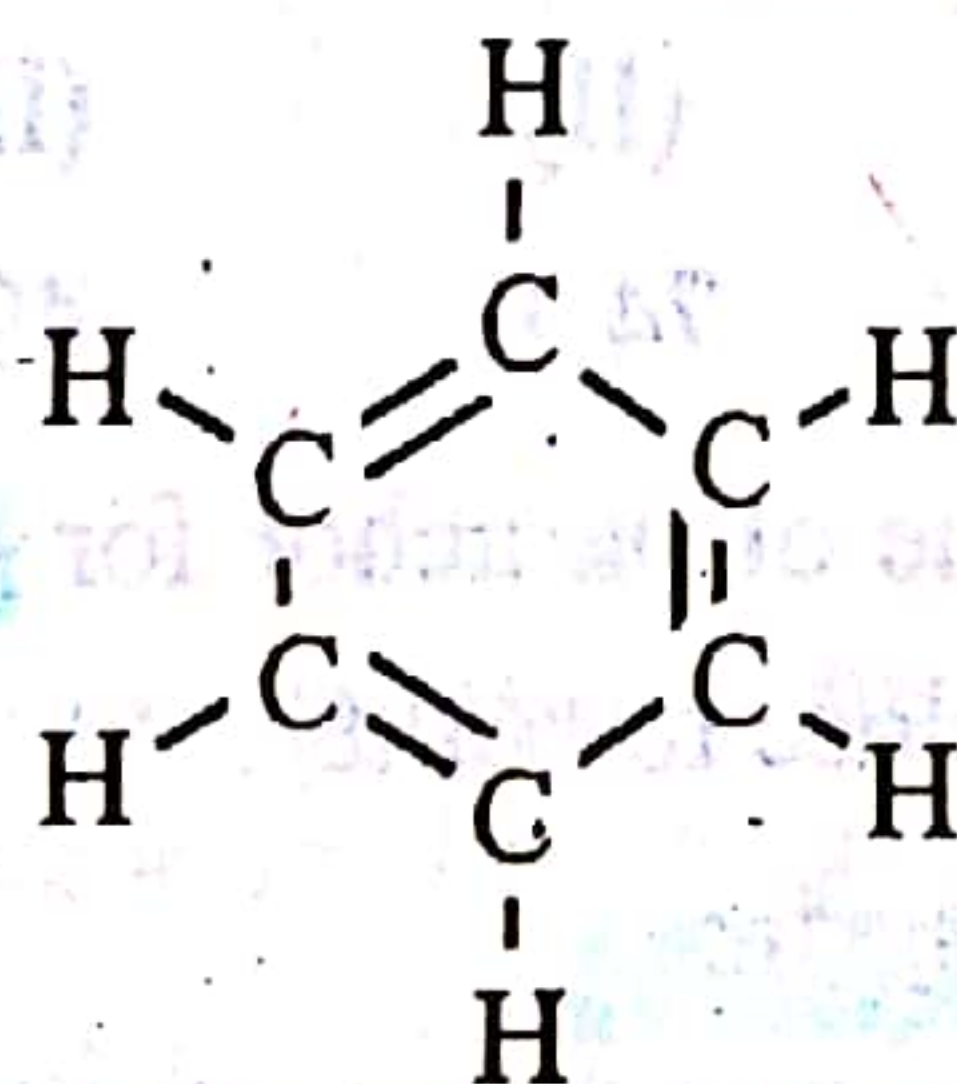
When we sum up the values of atomic parachors and structural parachors of benzene, keeping in view its cyclic structure i.e. number of double and single bonds, then it comes to be 206.9.
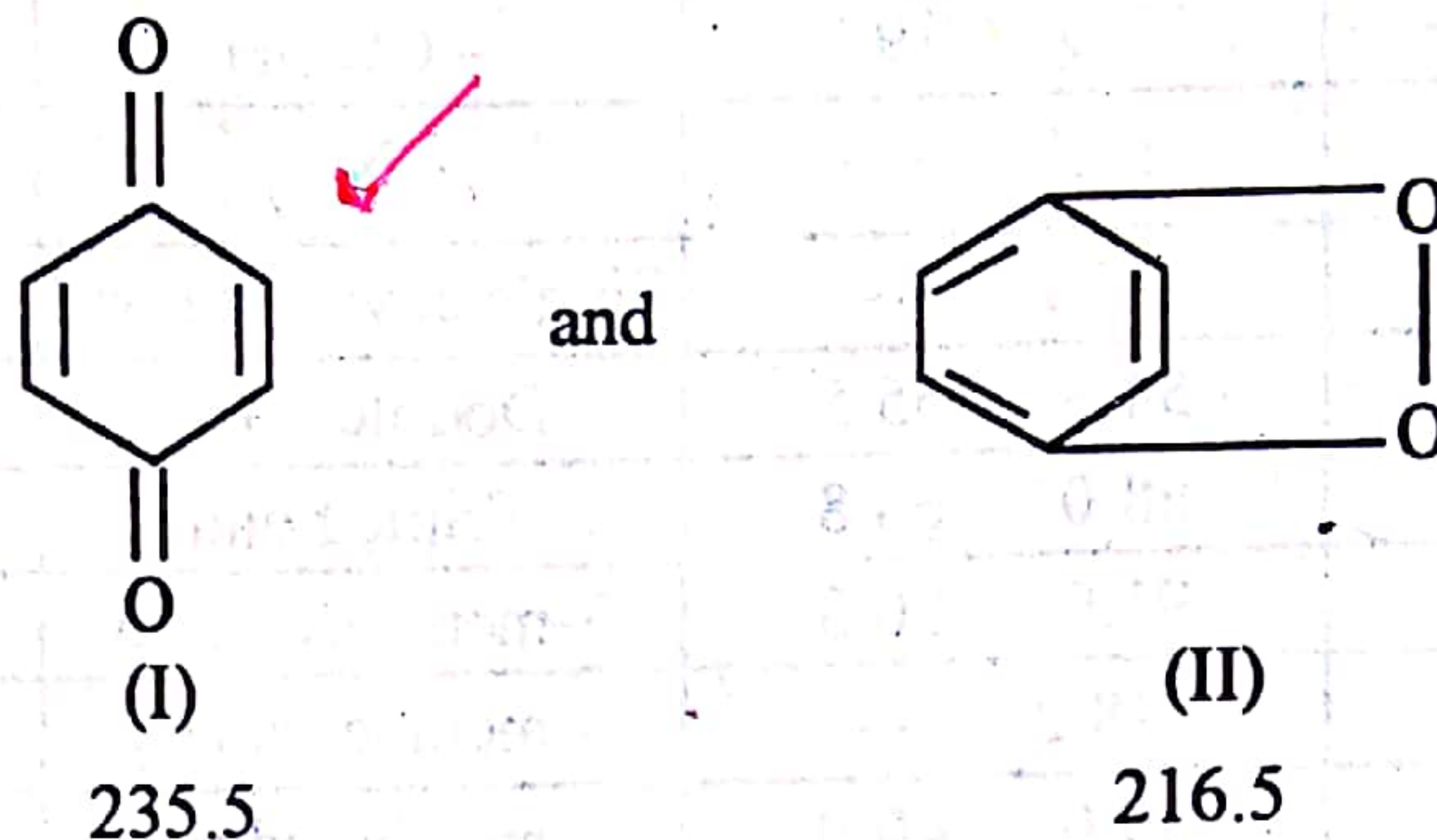
6 carbon atoms	6 × 8.6	= 51.6
6 hydrogen atoms	6 × 15.7	= 94.2
3 double bonds	3 × 19.9	= 59.7
Six membered ring		= 1.4
		= 206.9

The experimental value of the parachor determined from surface tension measurements is 206.7. These two values agree with each other. So, Kekule's structure is confirmed.

**(ii)   The Structure of quinone:**

Two possible structures have been proposed.

(I)	and	(II)
235.5		216.5

The addition of parachor equivalent from the above table for structure (I) is 236.1, while for structure (II), the theoretical value comes out to be 219. The observed value of parachor from surface tension measurements is 236.8. It means that structure (I) is very close to reality, and is the accepted structure.

**(iii)   The structure of nitro group:**

Nitro group can be written in many forms. Their theoretical parachor values by consulting the above table are shown below.

(I)	(II) ✓	(III)	(IV)
98.9	74.1	49.3	69.2
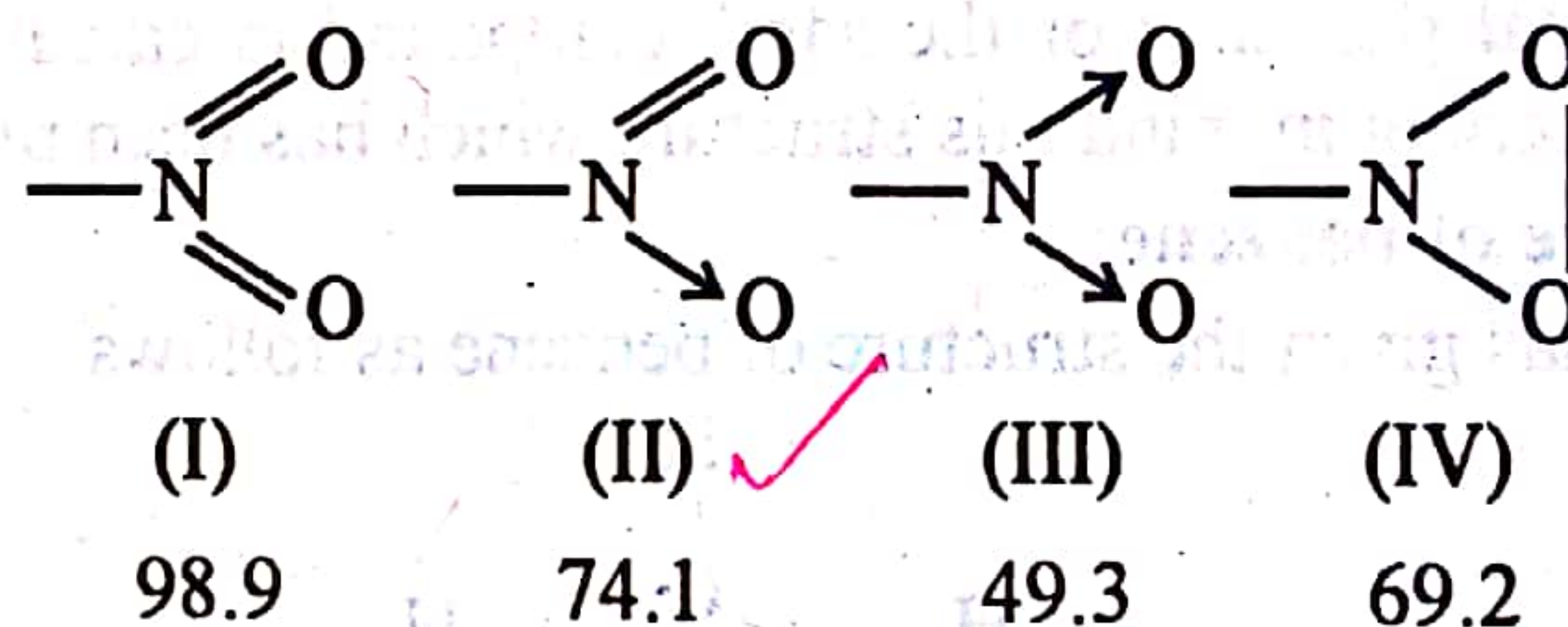
The experimental value of parachor for –NO$_2$ group varies from 73 to 75. It means that structure (II) is close to reality.

(iv)   Structure of paraldehyde:

Paraldehyde is a polymer of acetaldehyde. Its experimental and theoretical values differ from each other. The reason is that three carbonyl groups of acetaldehyde are no more there in the product. It means that carbon oxygen double bonds are not there in the products.

$$3CH_3 - C - H \longrightarrow$$

Paraldehyde
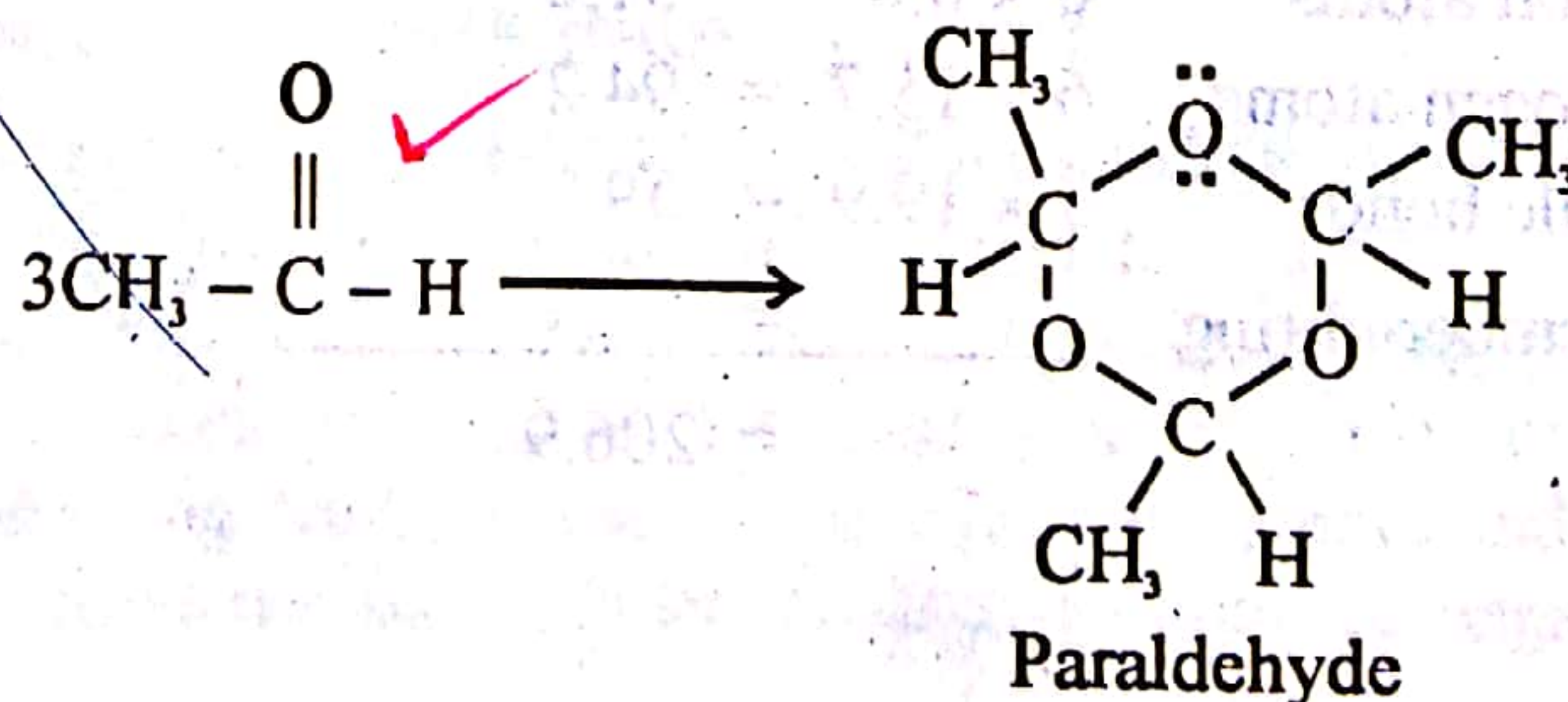
5.   **Structure of positional isomers:**

Disubstituted derivatives of benzene have three positional isomers, but their theoretical and experimental parachors are same. For example, the observed value of o-chlorotoluene is 280.8 and for p-chlorotolucne, the value is 283.6.

Moreover, the theoretically calculated value for both these compounds is 283.3. It means that, we can not distinguish betwr   positional isomers by parachor values.
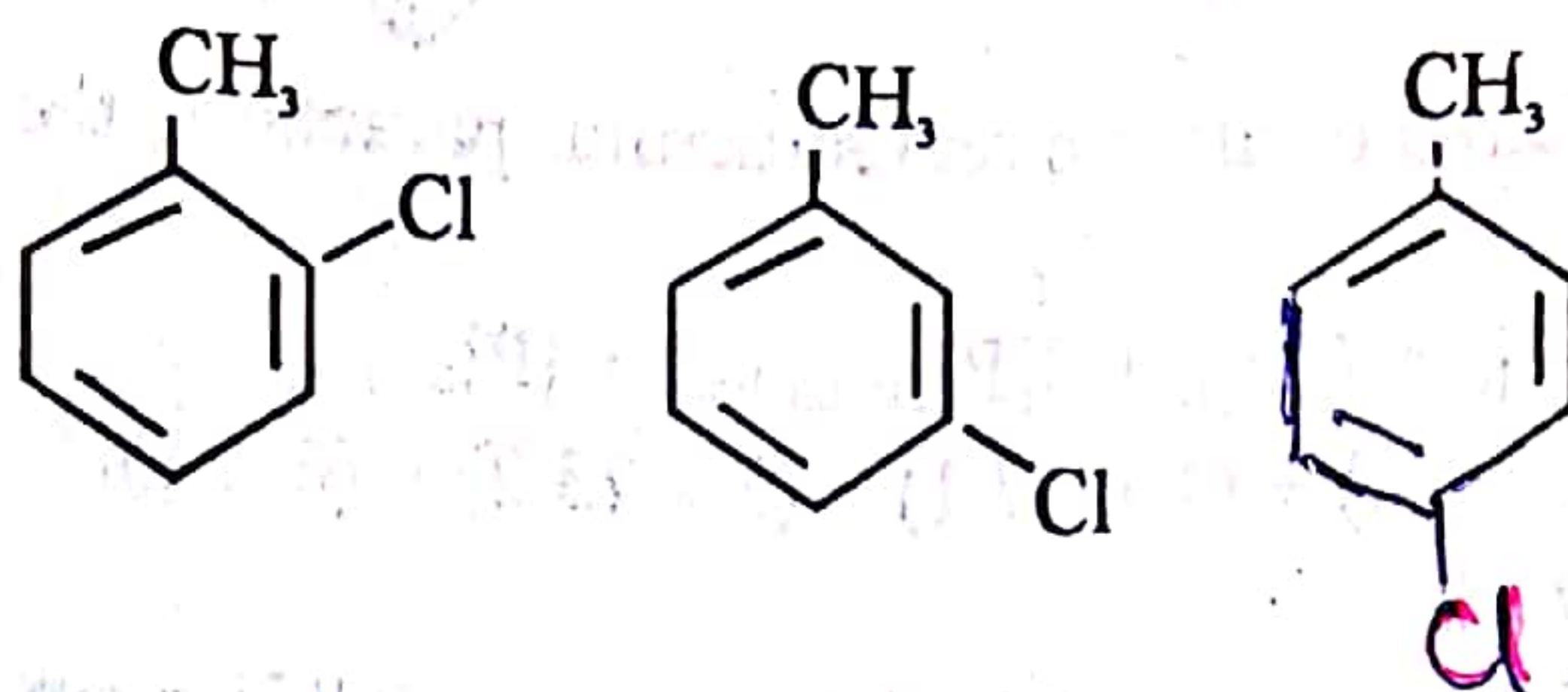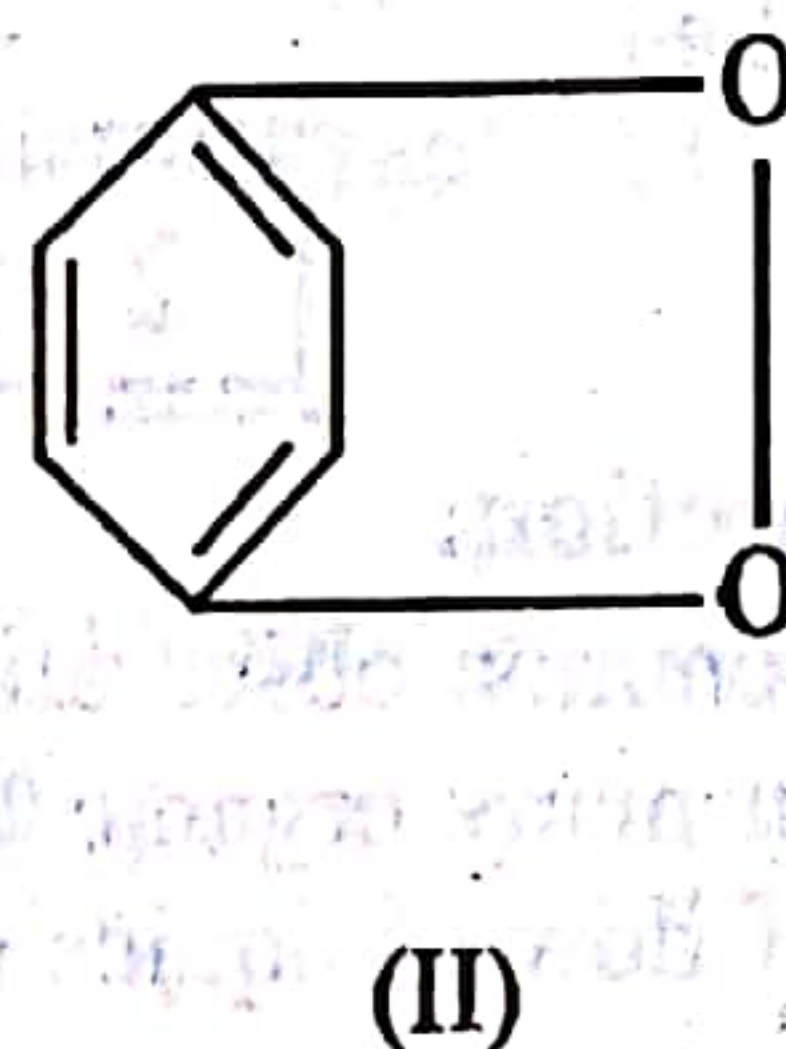

EXAMPLE (4)

How do you establish the structure of quinone based upon parachor values.

SOLUTION:

Following two structures for quinone are proposed. The molecular formula for quinone is $C_6H_4O_2$,

(I)   (II)

Theoretical parachor of quinone using the table of atomic and structural parachors. For structure (I), the theoretical parachor is

$$= 6[P]_C + 4[P]_H + 2[P]_O + 4[P]_{Double\ bond} + [P]_{6-ring}$$
$$= (6 \times 4.8) + (4 \times 17.1) + (2 \times 20.0) + (4 \times 23.2) + 6 \times 1$$
$$= 236.1$$

Similarly for structure (II), the theoretical parachor is

$$= 6[P]_C + 4[P]_H + 2[P]_O + 3[P]_{Double\ bond} + [P]_{6-ring}$$
$$= (6 \times 4.8) + (4 \times 17.1) + (2 \times 20.0) + (3 \times 23.2) + (2 \times 6 \times 1)$$
$$= \boxed{219.0} \quad \text{Ans.}$$

The experimental value of parachor is $= \boxed{236.8}$ Ans.

Experimental value is close to the value calculated for structure (I).

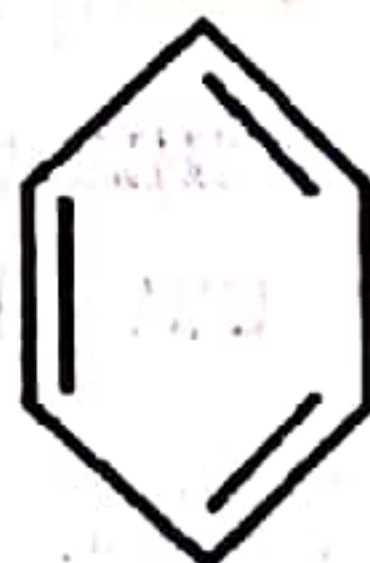Hence structure (I) may be the correct structure for quinone.

EXAMPLE (5)

Justify the structure of benzene, given in the literature, based on parachor values.

SOLUTION·

Kekule's structure for benzene (C_6H_6) is

Using the table of atomic and structural parachors, the theoretical value of parachor is,

$$= 6[P]_C + 6[P]_H + 3[P]_{Double\ bond} + [P]_{6-ring}$$
$$= (6 \times 4.8) + (4 \times 17.1) + (3 \times 23.2) + (6 \times 1)$$
$$= 207.1$$

Density of benzene at 20°C, (D) $= 0.878 \text{ g cm}^{-3}$
Surface tension of benzene at 20°C, (γ) $= 29.3 \text{ dynes cm}^{-1}$
Molecular weight of benzene (C_6H_6) $= 78 \text{ g mol}^{-1}$

Experimental value of parachor, (P) $= \dfrac{M\gamma^{1/4}}{D}$

$$= \dfrac{78 \times (29.3)^{1/4}}{0.878} = \boxed{206.7} \text{ Ans.}$$

The experimental value agrees with the calculated value. Hence Kekule's structure is justified.

<div style="text-align:center">

2.4.0 VISCOSITY

</div>

[margin note: → Honey
→ mobile oil]

2.4.1 Introduction:

It is a common observation that the thick liquids like honey and mobile oil, flow slowly than many organic liquids like benzene and toluene etc. It means that different rates of flow of liquids depend upon certain property and that is viscosity.

Viscosity is the property which opposes the relative motion of adjacent layers. In order to understand the viscosity. Let us consider the flow of a liquid as shown in the following diagram (9). Liquid is considered to be arranged in a large number of parallel layers. The layer adjacent to the walls of the tube is stationary. When we move towards the centre of the tube, then the velocities of the successive layers go on increasing.

When the steady flow is reached then velocity difference between any two layers becomes constant.
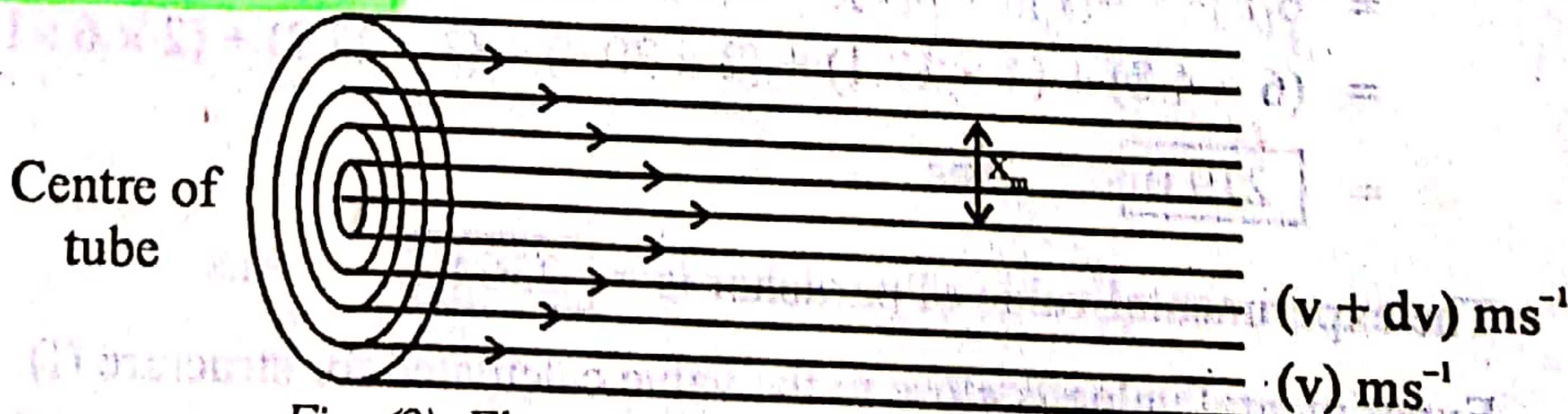

Centre of tube

$(v + dv) \text{ ms}^{-1}$
$(v) \text{ ms}^{-1}$

Fig. (9) Flow of a liquid through a narrow tube.

The force which is required to maintain the steady flow of liquid in direction of the force is directly proportional to the velocity gradient which is normal to the direction of flow. It is also proportional to the area of the contact 'A' between the moving layers of the liquids.

In C.G.S system, the unit of 'η' is expressed as g cm^{-1} sec^{-1} and it is called poise.

Velocity gradient

$$A = \text{Area of contact}$$

$$\frac{dv}{dx} = \text{Velocity gradient}$$

$$F \propto -A\frac{dv}{dx}$$

$$\text{or} \quad F = -\eta A\frac{dv}{dx} \quad \quad \ldots\ldots (1)$$

$$\eta = -\frac{F}{A \cdot \frac{dv}{dx}} \quad \quad \ldots\ldots (2)$$

$$\eta = \text{co-efficient of viscosity or simply called viscosity.}$$

2.4.2 Definition and units of η:

"It is the force per unit area, needed to maintain unit difference of velocity between two parallel layers of the liquid, unit distance apart."

The units of viscosity 'η' can be derived from the equation (1)

$$\eta = \frac{F}{A} \times \frac{dx}{dv} = \frac{\text{force}}{\text{area}} \times \frac{\text{distance}}{\text{velocity}}$$

Since J = kg ms^{-2}, so, force = mass × length × time^{-2}

$$\eta = \frac{\text{mass} \times \text{length} \times \text{time}^{-2}}{(\text{length})^2} \times \frac{\text{length}}{\text{length/time}}$$

$$\eta = \text{mass} \times \text{length}^{-1} \times \text{time}^{-1}$$

In SI units η is in kg m^{-1} s^{-1}

$$\text{1 poise} = 10^{-1} \text{ kg m}^{-1} \text{ s}^{-1} = 0.1 \text{ kg m}^{-1} \text{ s}^{-1}$$

Unit of viscosity "Poise":

"When a force of one dyne per square cm is maintained, between two layers which are 1 cm apart and the difference of velocity between the two layers is 1 cm per second, then it is called poise."

$$\text{1 centipoise} = 10^{-2} \text{ poise}$$

$$\text{1 millipoise} = 10^{-3} \text{ poise}$$

Fluidity:

"Fluidity is the reciprocal of viscosity."

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

The units of fluidity are reciprocal of viscosity i.e. (Poise)$^{-1}$.

2.4.3   Effect of temperature on viscosity:

The increase of temperature increases the kinetic energy of molecules of liquids. It means that a liquid starts flowing faster at high temperatures. In other words, viscosity of a liquid falls with the increase in temperature. It is estimated that for each one degree rise of temperature, there is 2% decrease of viscosity.

Mathematical relationship:

Arrhenius has given the following relationship between viscosity and temperature.

$$\eta = Ae^{B/RT} \qquad \qquad \text{...... (1)}$$

A and B are the constants depending upon the nature of liquid. According to this equation, increase of temperature decreases the viscosities of liquids. If we want to determine the constant 'A' and 'B' then we can convert it into the equation of a straight line by taking the natural log i.e. log to the base e. (It can be written as ln)

$$\log_e \eta = \log_e A + \frac{B}{RT} \qquad \qquad \text{...... (2)}$$

$$\log_e \eta = \frac{B}{R} \cdot \left(\frac{1}{T} \right) + \log_e A \qquad \qquad \text{...... (3)}$$

If we plot a graph between $\frac{1}{T}$ on x-axis and $\log_e \eta$ (ln η) on y-axis, then a straight line is obtained. From the slope of the straight line 'B' can be calculated and from the intercept of the straight line factor 'A' can be calculated.

The following graphs of Fig. (10) show that many of liquids show the straight lines. The anomalous behaviour of H_2O is seen from the graph, because its hydrogen bonded structure is broken with the rise of temperature. The quantity 'B' is the activation of energy for the viscous flow. It is the energy barrier which must be overcome before the flow can occur. It means that a molecule of a liquid should gain sufficient energy to push aside the surrounding molecules before it can take part in the liquid flow.
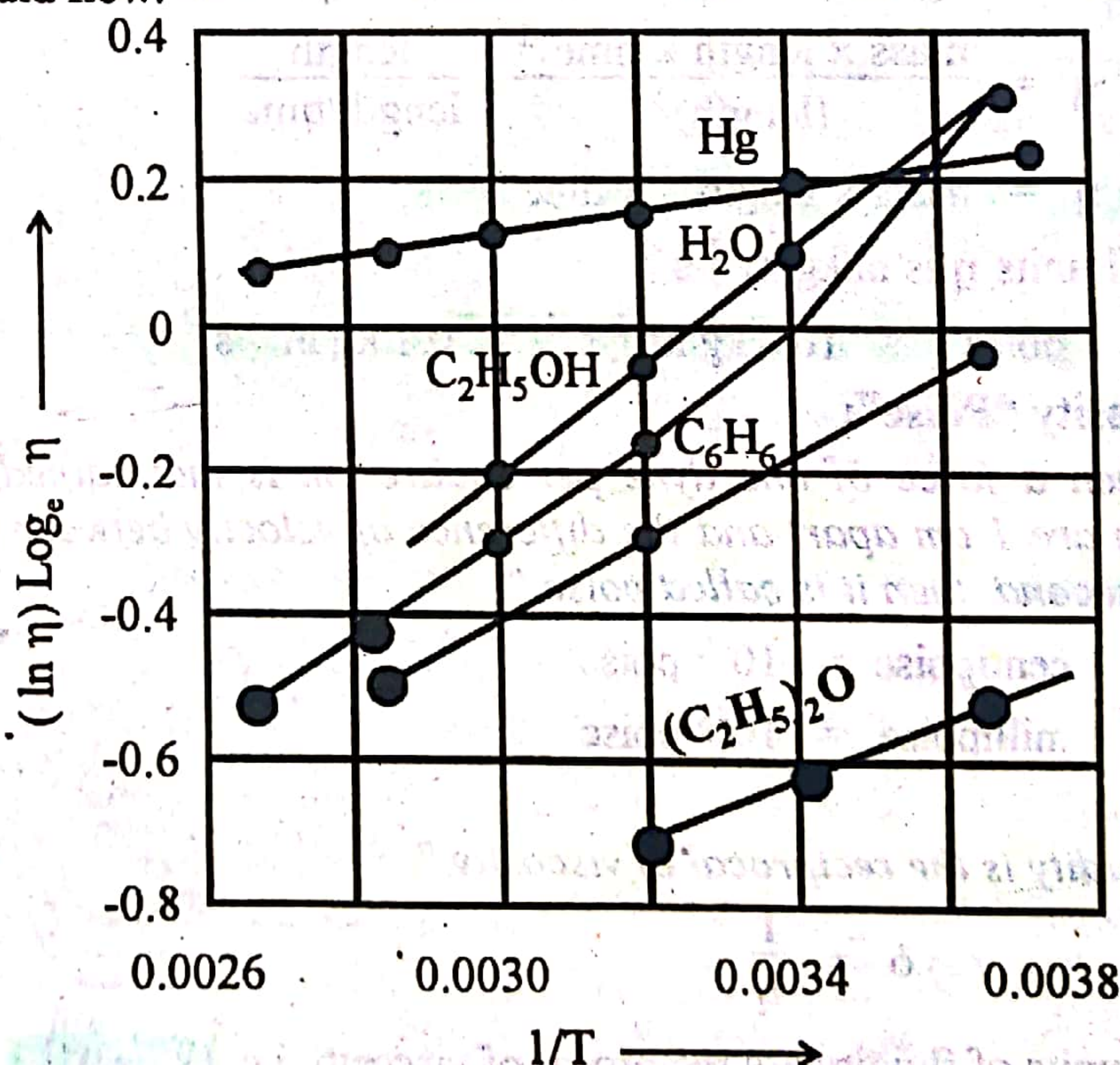

Fig. (10) *The dependence of viscosity on temperature log$_e$ η versus 1/T.*

Viscosities of some important liquids:

Table (3): Co-efficients of viscosity of liquids at 20°C in Poise and in SI units (kg m^{-1} sec^{-1})

Liquid	Viscosity (C.G.S. units) poise	Viscosity (SI units) kg m^{-1} s^{-1}
Benzene	0.00652	0.000652
Carbon tetrachloride	0.00969	0.000969
Ethanol	0.01200	0.001200
Ether	0.00233	0.000233
Glycerin	14.9	1.49
Water	0.0101	0.00104

2.4.4 Measurement of viscosity:

General Principle:

The measurement of viscosity of liquid is based on Pioseulle's equation (4)

$$\eta = \frac{\pi P t r^4}{8 Vl} \qquad \dots\dots (4)$$

Where,

V = Volume of liquid.

r = Radius of capillary tube

l = Length of the tube.

t = Time of flow in seconds.

P = Pressure applied.

We should keep it in mind that, equation (4) applies to the liquids, when the rate of flow is slow and steady. The flow should be stream line. Moreover, the diameter of the tube should be very small. If the flow rate is higher and the diameter of the tube is large, then flow becomes turbulent.

In order to decide, that which type of flow is there, we should use the empirical equation called Reynold's number. It is dimensionless quantity and its formula is as follows.

$$\text{Reynold's number} = \frac{2 r \bar{v} d}{\eta}$$

r = Radius of tube.

d = Density of liquid.

η = Co-efficient of viscosity.

$\bar{v}$ = Average velocity of liquid.

It is found that, if the Reynold's number is equal or less than 2000, then the flow is streamlined. If the value is greater than 4000, then the flow is turbulent.

2.4.5 Measurement of absolute viscosity:

It is difficult to measure directly the value of absolute viscosity of a liquid using equation (1). The reason is that the measurement of 'P', 'r' and 'V' is difficult, so the viscosities of liquids are expressed in relative terms. *"This is the ratio of viscosity of the liquid to the viscosity of water taken as reference standard and this is called relative viscosity."*

2.4.6 Measurement of relative viscosity:

Ostwald's viscometer is used as shown in following diagram (11).
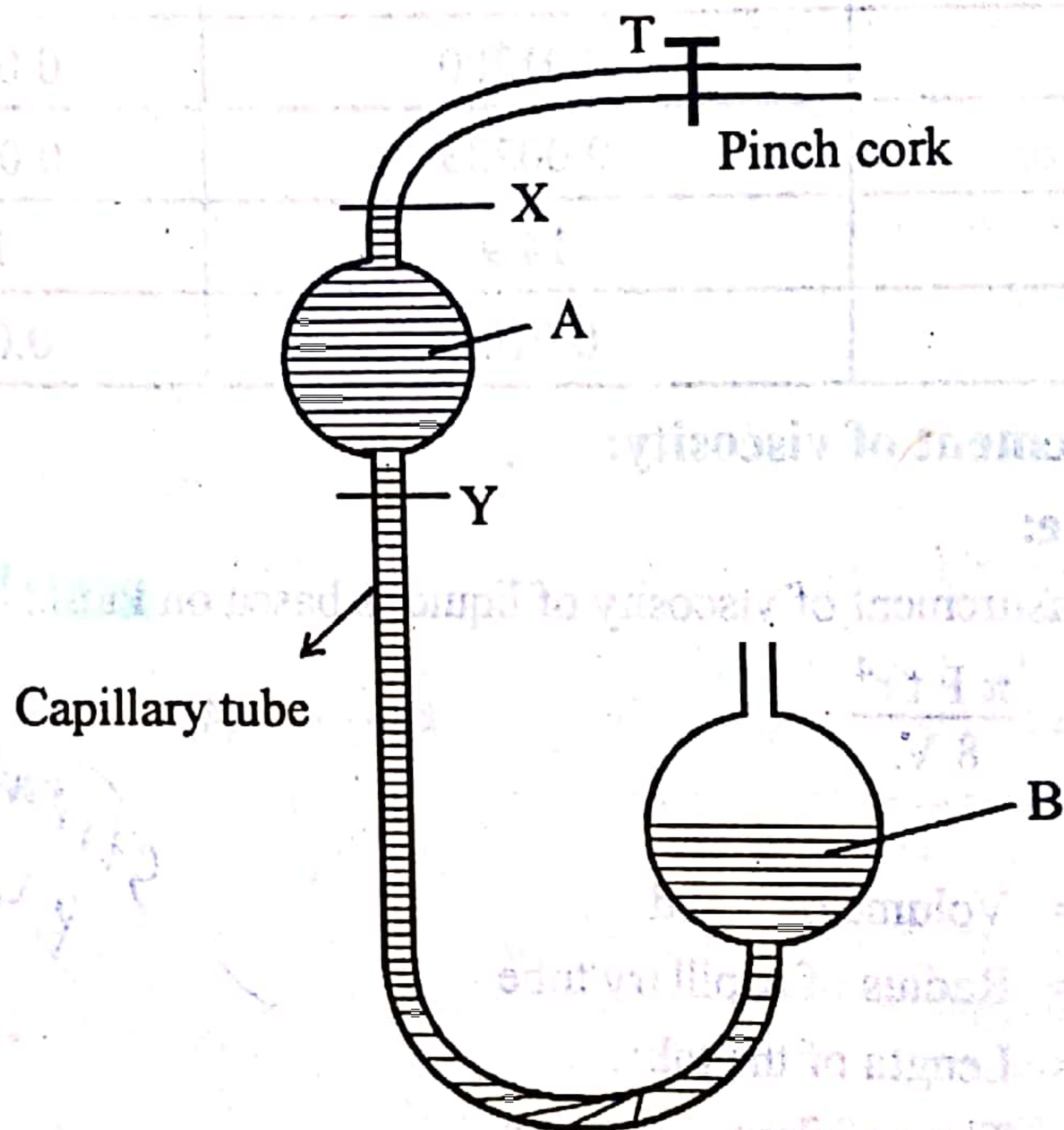
Fig. (11) Ostwald's viscometer to measure the relative viscosity of a liquid.

It is a U-shaped glass tube with two marks 'x' and 'y'. It has two bulbs as 'A' and 'B'. The bulb 'A' is at higher level than 'B'. A definite volume of liquid is put in bulb 'B' and then sucked in bulb 'A'. The time of flow of the liquid through the capillary tube is noted. Similarly, the time of flow of reference liquid water is also noted. Density of the liquid is determined by specific gravity bottle. Following equation is applied to calculate 'η_1', if we know all other five factors.

$$\frac{\eta_1}{\eta_2} = \frac{d_1}{d_2} \times \frac{t_1}{t_2} \qquad \qquad \cdots \cdots (5)$$

$\eta_1 = $ viscosity of liquid

$\eta_2 = $ viscosity of reference liquid

$d_1 = $ density of liquid, determined by specific gravity bottle

$d_2 = $ density of reference liquid taken from literature

$t_1 = $ time of flow of liquid

$t_2 = $ time of flow of reference liquid

EXAMPLE (6)

The time of flow of water through an Oswald viscometer is 90 seconds while for the same volume of ethyl alcohol, the time is 135 seconds. The absolute viscosity of water is 1.005×10^{-3} kg m^{-1}s^{-1} at 20°C. Densities of water and ethyl alcohol are 0.9982×10^{-3} kg m^{-3} and 0.80×10^{-3} kg m^{-3}, respectively at 20°C. Calculate the relative and absolute viscosities of C_2H_5OH at 20°C.

SOLUTION:

Data:

$$t_{alc} = 135 \text{ sec}$$
$$t_{H_2O} = 90 \text{ sec}$$
$$\eta_{H_2O} = 1.005 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$$
$$d_{alc} = 0.80 \times 10^{-3} \text{ kg m}^{-3}$$
$$d_{H_2O} = 0.9982 \times 10^{-3} \text{ kg m}^{-3}$$
$$\eta_{alec} = ?$$

$$\text{Relative viscosity} = \frac{\eta_{alc}}{\eta_{H_2O}} = \frac{d_{alc} \, t_{alc}}{d_{H_2O} \, t_{H_2O}}$$

Putting values

$$\text{Relative viscosity} = \frac{0.80 \times 10^{-3} \times 135}{0.998 \times 10^{-3} \times 90} = 1.2202$$

Absolute viscosity, $\eta_{alc} = 1.2202 \times \eta_{H_2O} = 1.202 \times 1.005 \times 10^{-3}$ kg m^{-1} s^{-1}

$$= \boxed{1.208 \times 10^{-3} \text{ kg m}^{-1} \text{s}^{-1}} \quad \text{Ans.}$$

2.4.7 Viscosity and constitution:

Viscosity surely depends upon the structure of the compound. Following various aspects are very important to be considered.

(1) In homologous series of organic compounds the members differ from each other by '– CH$_2$' group. It has been observed that there is gradual increase of viscosity values for the members of homologous series.

(2) Some of the liquids are associated and so their viscosities increase. Dunston in 1909, gave a useful relationship.

$$\frac{d}{M} \times \eta \times 10 = 40 \text{ to } 60 \quad \text{(in S.I. units)}$$

For the associated liquids the values come out to very higher than 60. If d, M and η are measured in C.G.S. units, then following equation is used.

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

Following table (4) shows that water, glycol and glycerol are associated liquids.

Table (4) Values of $\frac{d}{M} \times \eta \times 10^6$

Liquid	$(d/M) \times \eta \times 10^6$	Conclusion
Acetone	43	Unassociated
Toluene	56	"
Benzene	73	"
Water	559	Associated
Glycol	2750	More associated
Glycerol	116400	Highly associated

(3)   Viscosity also depends upon the shape of the molecules. If the chain length of the molecule is shorter, then viscosity is less. The compounds of normal chain length have usually greater viscosity values than branched chain isomers. Similarly, the viscosities of trans isomers are greater than cis-isomers.

(4)   The strength of intermolecular forces can also be depicted from the values of viscosity.

(5)   Water has a greater viscosity than ethyl alcohol due to greater hydrogen bonding in it.

(6)   Just like the parachor of liquid, a parameter called Rheochor is also additive and constitutive property. It depends upon viscosity of the liquid.

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

We can verify the structure of the compound by comparing theoretical and experimental rheochors. Table (5)

Table (5) Atomic and Structural Rheochors

Atom		Rheochor	Linkage	Rheochor
Carbon		12.8	Covalent bond	0.0
Oxygen (in ether)		10.0	Coordinate bond	0.4
(in ketone)		13.2		
Hydrogen	(in C – H)	5.5	6-membered ring (sat)	–5.6
	(in C – OH)	10.0	— CH₂	23.6
	(in HCl)	9.7	— C₆H₅	100.7
	(in HBr)	12.6	—C(=O)O	36.0
	(in HI)	15.0	— NH₂	20.6
Chlorine		27.3	> NH	13.6
Bromine		35.8	CN	33.0
Iodine		47.6		
Nitrogen		6.6		

2.4.8 Measurement of molar mass of polymer:

Molar masses of polymers are very high. It depends upon the reaction conditions whether the molar mass of the polymer is high or low. The measurement of viscosity of solutions of polymers can help us to find the molar masses.

Following relationship is used for this purpose

$$[\eta]_{int} = KM^a$$

$[\eta]_{int}$ = Intrinsic viscosity

M = Molar mass of polymer

K and a = Constants, depending upon the nature of solvent and the polymer.

a = Factor depending upon the shape of molecule.

For example, for random coiled molecules,

a = 0.5

For rod like molecules

a = 2

For spherical coiled molecules

a = 0

Intrinsic viscosity is a limiting viscosity number, when the concentration of the polymer solution approaches zero.

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0}$$

η = Viscosity of a solution of polymer in solvent

η_0 = Viscosity of pure solvent

A graph is plotted between concentrations of various solutions on x-axis and η_{sp}/c on y-axis. A straight line is obtained. This graph is extrapolated to the limiting value, when c → 0. The value of η_{sp}/c having the value at that stage is called $\eta_{intrinsic}$.

2.5.0 REFRACTIVE INDEX

2.5.1 Introduction:

"When a ray of light enters from one medium to the other, then it changes its direction. This property of light is called refraction."

When a ray of light travels from air or vacuum to a denser medium say solid or a liquid, then ray of light bends towards the normal. This is shown in the following diagram. (12)
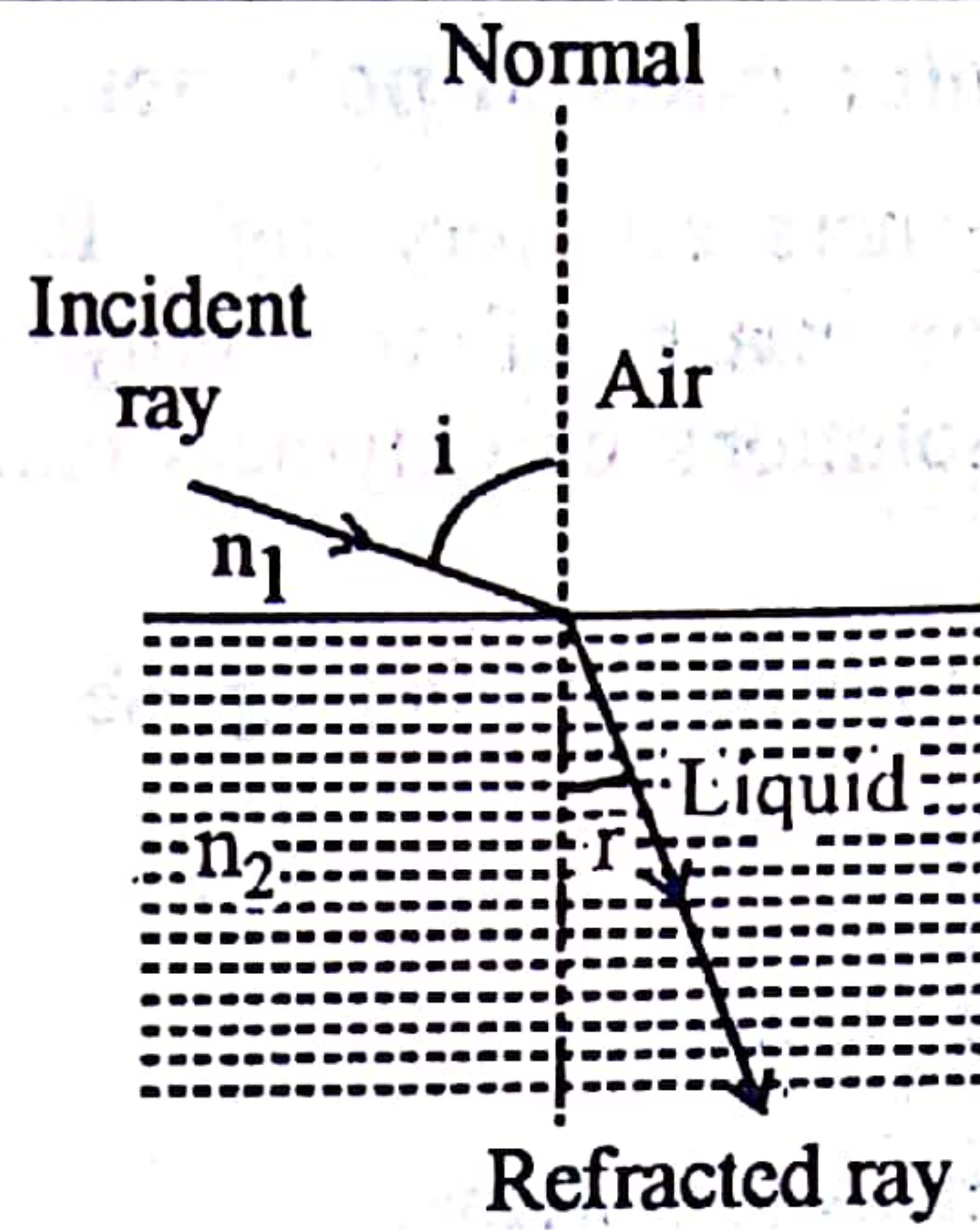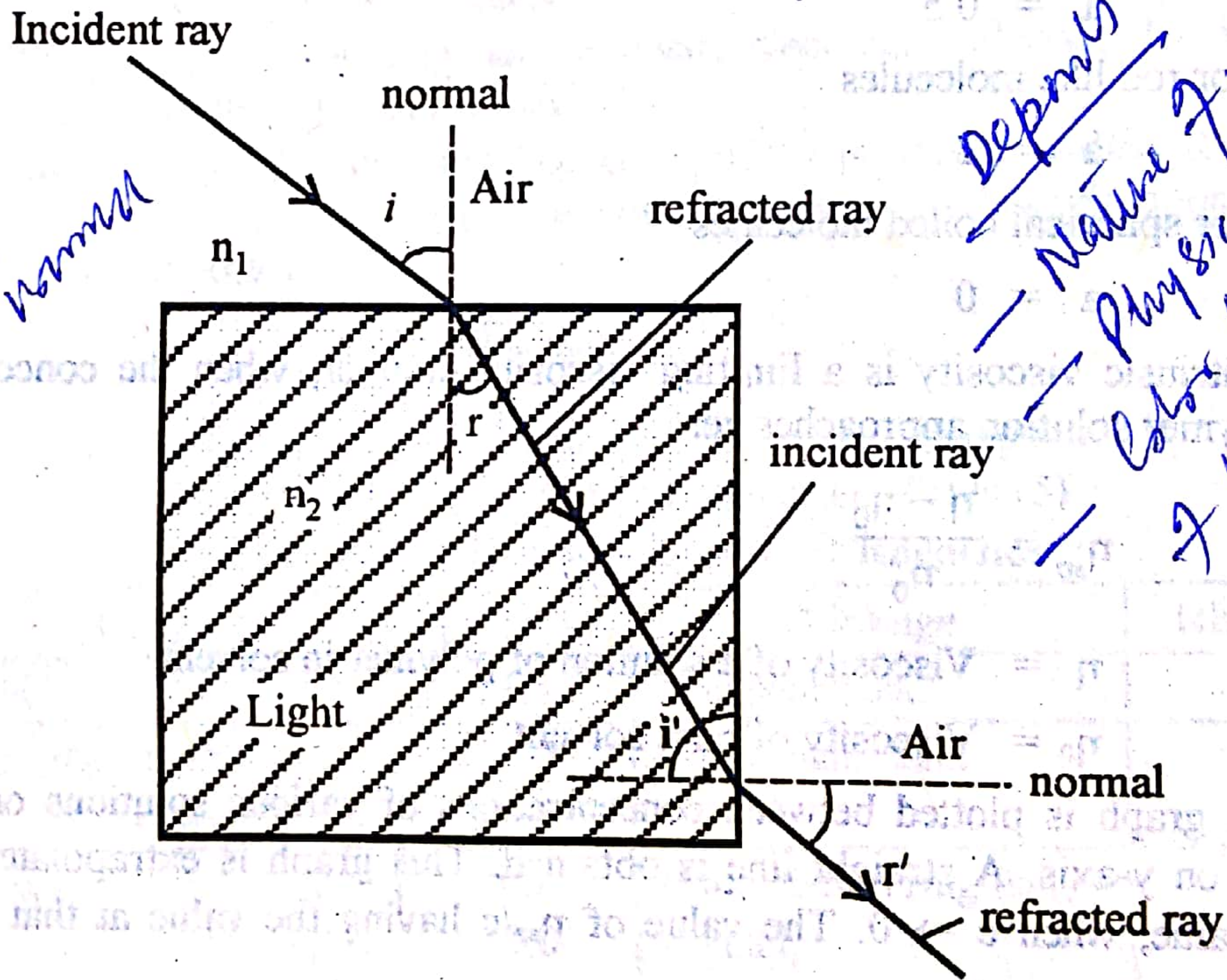
Fig. (12) Refraction of light.

When the angle of incidence 'i' is increased, then angle of refraction 'r' also increases. Anyhow, the value of r always remains smaller than 'i'. If the ray enters from denser to the rarer medium, then it bends away from the normal. The angle of incidence is less than the angle of refraction as shown in the following diagram. (13)

Fig. (13) How the image in displaced due to refraction.

It means that, if the ray of light enters into the denser medium and then emerges out on the other side of the rarer medium, then the ray is displaced. This diagram explains that a image is displaced due to refraction.

2.5.2 Snell's law:

According to this law, the ratio of sine of the angle of incidence to the sine of angle of refraction is a constant quantity.

$$n = \frac{\sin i}{\sin r} = \frac{\text{velocity in the air (medium of angle i)}}{\text{velocity in the liquid (medium of angle r)}}$$

Actually the angle of incidence is different from the angle of refraction due to the reason that the velocity of the light in the two media is different. According to the law of refraction,

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

n_1 = Refractive index of the rarer medium

n_2 = Refractive index of the denser medium.

2.5.3 Critical angle of refraction:

When the angle of incidence increases, then the angle of refraction also increases. When the angle of incidence is equal to 90°, then the 'r' approaches to its maximum value as shown in the following diagram (14).
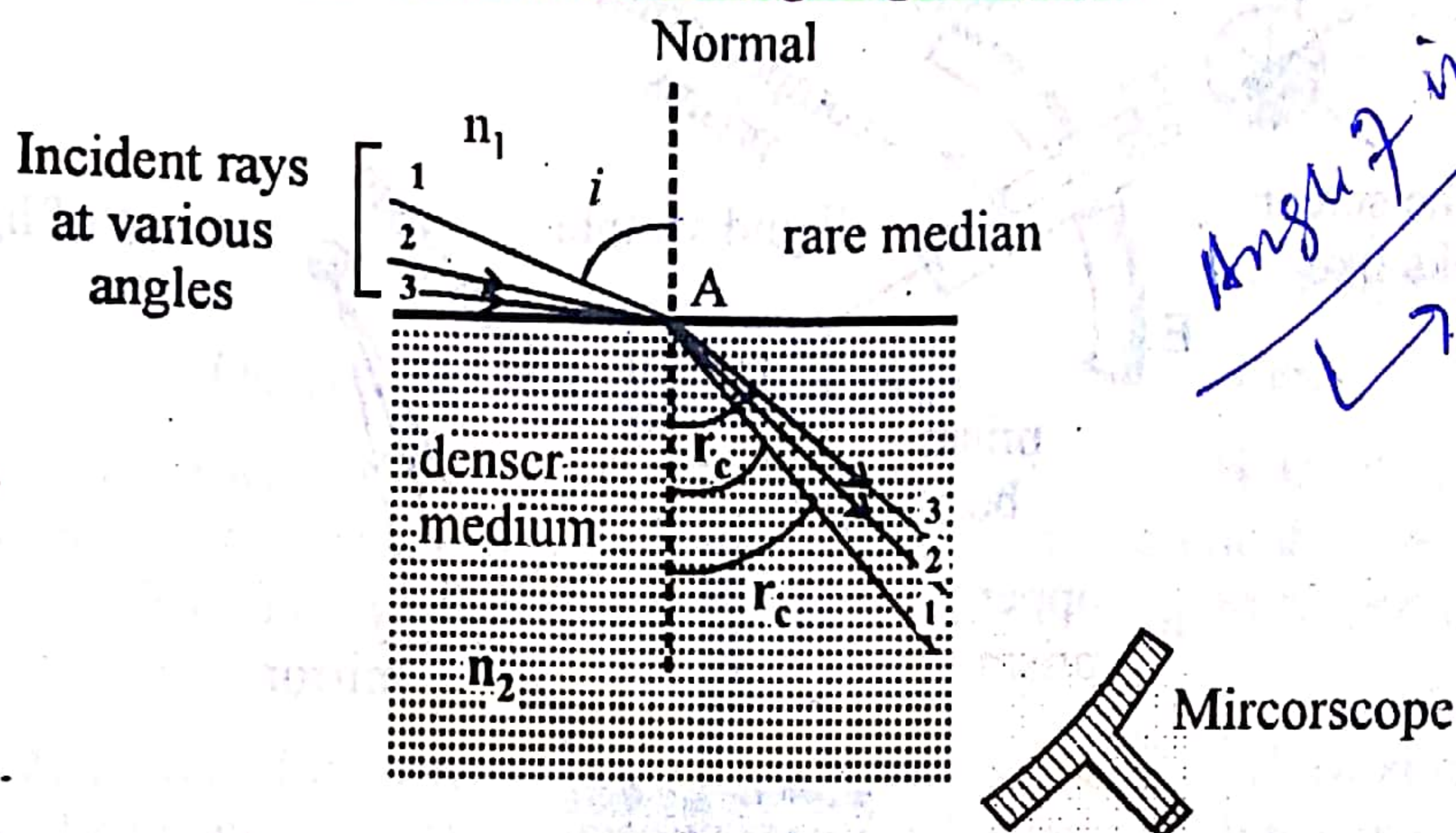

Fig. (14) The principle of critical angle of refraction.

At this time the angle of refraction is called critical angle of refraction, denoted by 'r_c'. Since, at this stage i = 90°

$$\sin i = \sin 90 = 1$$

Hence, $$\frac{1}{\sin r_c} = \frac{n_2}{n_1}$$

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

If the rarer medium is air or vacuum, then its refractive index $n_1 = 1$,

$$\frac{1}{n_2} = \sin r_c$$

$$n_2 = \frac{1}{\sin r_c}$$

It means that the refractive index of the denser medium (n_2) can be obtained, if we take the reciprocal of sine of critical angle of refraction. This critical angle of refraction is obtained by adjusting the angle of incidence at 90°.

2.5.4   Measurement of refractive index:

. There are two methods which are mostly employed, for the measurement of refractive index of liquids.

(i)   Measurement with Abbe's refractometer.

(ii)   Measurement with Pulfrich refractometer.

(i)   **Abbe's refractometer:**

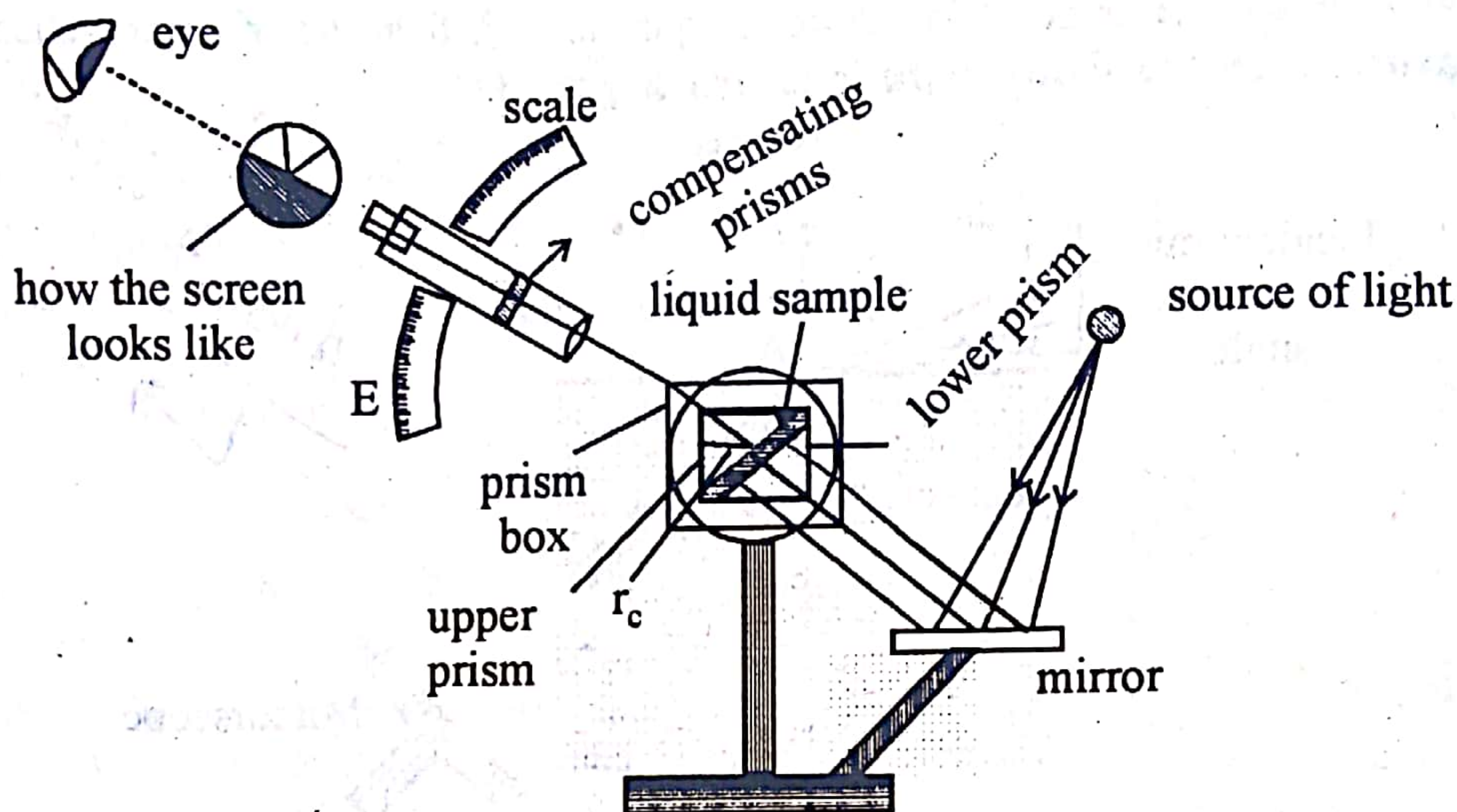This apparatus is as shown in the following diagram. (15)

Fig. (15) Abbe's refractometer for measurement of refractive index.

A thin film of the liquid is placed between two prisms. Light is allowed to enter on the lower side of the lower prism. Sodium 'D'-line can also be used. The surface of the lower prism acting as hypotenues is ground very nicely. For this reason the light enters the liquid at all angles of incidence.

Actually, no ray of light can enter the upper prism with greater angle of refraction than grazing incidence. The angle of grazing incidence means which is less than 90°. In this way, the view in the telescope appears to be divided into two bands. One band is bright and other is dark. The assembly of the prism is rotated with the help of side knob, till the cross wire of the telescope coincides with the edge of the bright band. The reading of the refractive index can be done directly from scale.

(ii)   **Pulfrich refractometer:**

This is more accurate method for measurement of refractive indices of liquids. Following arrangement (16) is helpful to understand the principle and working of Pulfrich refractometer.
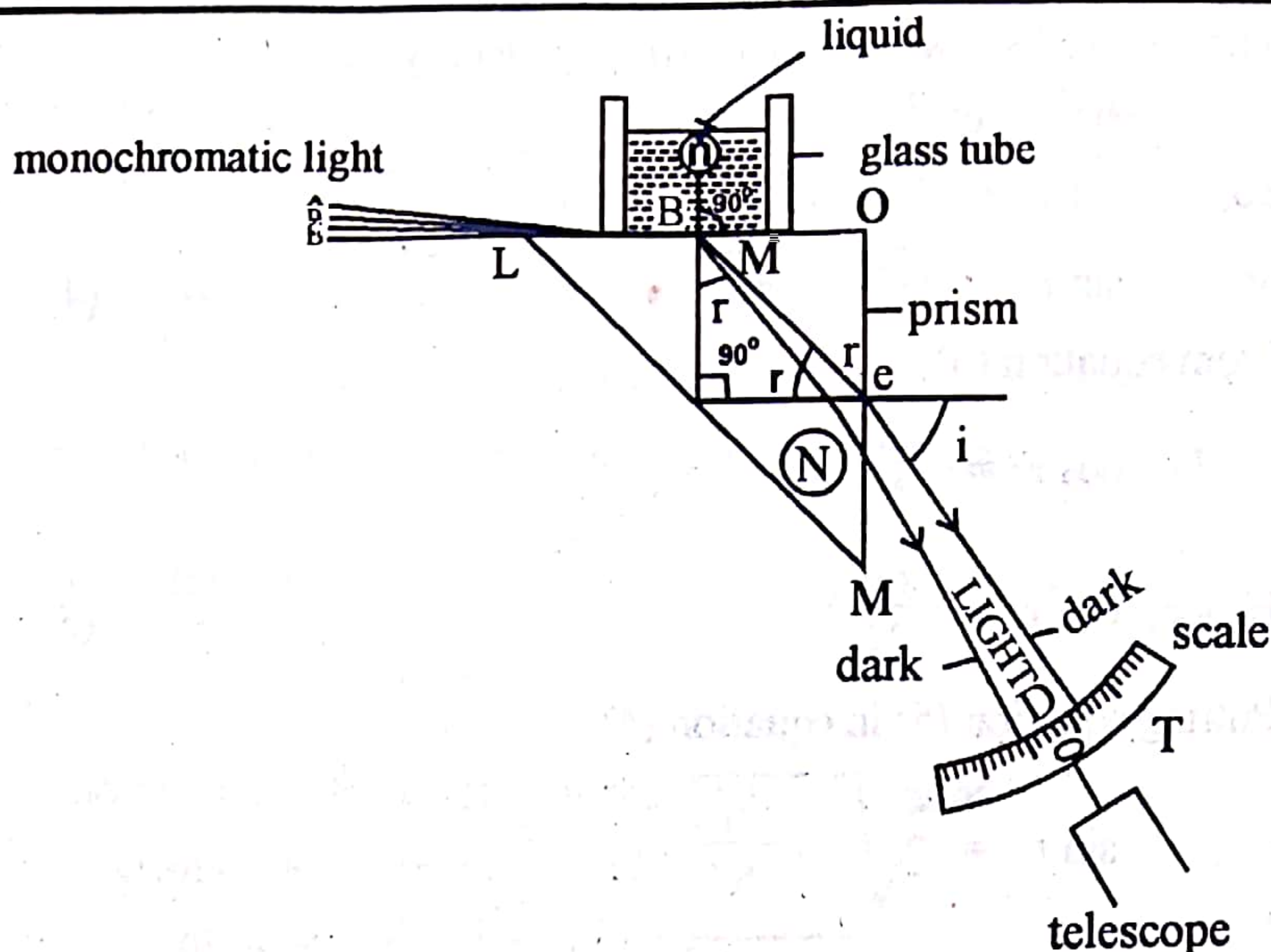
Fig. (16) The optical system of Pulfrich refractometer.

This refractometer has right angled glass prism, L M O. A glass cell is attached on its upper side. This glass cell is filled with that liquid whose refractive index is required. Refractive index of the prism should be greater than that of the liquid.

A source of monochromatic light is managed and it is allowed to enter the liquid at the grazing incidence, along the surface between the liquid and the prism. The path of the ray is shown by the ABCD and enters the telescope 'T'. The angle of incidence in the air is high and its angle of refraction is $(90° - r)$.

If the telescope is moved to make an angle less than 'i', then no ray of light will enter it and the field of view will be dark. When the telescope makes an angle greater than 'i' then field of view appears bright. It means that the accurate determination of the angle 'i' can be made at with the sharp boundary dividing a dark and a bright field of view and it can be observed through the telescope.

Let the refractive index of the liquid is 'n' and the refractive index of the glass prism is 'N'.

So, $$\sin r = \frac{n}{N} \qquad\qquad ...... (1)$$

The above diagram also shows that,

$$\frac{\sin i}{\sin (90° - r)} = N \qquad\qquad ...... (2)$$

Since, $\sin (90° - r) = \cos r$

Hence, equation (2) becomes

$$\frac{\sin i}{\cos r} = N \qquad\qquad ...... (3)$$

There is well known trigonometrically identity that,

$$\sin^2 r + \cos^2 r = 1$$

So, $\sin^2 r = 1 - \cos^2 r$

or $\sin r = \sqrt{1 - \cos^2 r}$ ...... (4)

From equation (3),

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

Hence, $\cos^2 r = \dfrac{\sin^2 i}{N^2}$ ...... (5)

Putting equation (5) in equation (4)

$$\sin r = \sqrt{1 - \frac{\sin^2 i}{N^2}}$$

$$\sin r = \sqrt{\frac{N^2 - \sin^2 i}{N^2}}$$

So, $N \sin r = \sqrt{N^2 - \sin^2 i}$

Since, $N \sin r = n$

Hence $n = \sqrt{N^2 - \sin^2 i}$ ...... (6)

With the help of equation (6), we can calculate the refractive index of the liquid 'n', if we know the refractive index of prism 'N' and the angle of incidence 'i', at which the light emerge from the prism. Sometimes, a table for the values of $\sqrt{N^2 - \sin^2 i}$ for different values of 'i' is supplied by the manufacturer of the instrument.

Mostly, the monochromatic light of sodium D-line is used and that is why this refractive index is denoted by n_D.

2.5.5 Refractive index and constitution:

The refractive index of a liquid changes with the change of the wave length of the light and also with the temperature. It means that when we mention the refractive index of liquid, we have to mention the temperature as well.

Specific Refraction or Refractivity:

In order to eliminate the effect of temperature, Lorentz and Lorenz in 1880, derived a relationship between refractive index of the liquid and density of the liquid.

$$R = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d}   \quad\quad ...... (7)$$

'R' is called specific refraction or refractivity. This parameter is independent of temperature. When the temperature of the liquid changes, then the values of 'n' and 'd' change in such a way that, the 'R' remains the same.

2.5.6 Molar refraction:

"*When refractivity is multiplied with the molar mass of the substance, then we get molar refractivity or molar refraction.*" This is denoted by 'R_m'.

$$R_m = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} \qquad \cdots\cdots (8)$$

'R_m' is also independent of temperature but depends upon the wavelength of the light used. Due to this reason, molar refractions are generally reported for definite wavelength.

2.5.7 Units of refractivity:

Since, $$R = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d}$$

'n' has no units. So, the units of R are the reciprocal of density.

Units of density $= $ g cm^{-3} or kg m^{-3}

So, the units of 'R' $=$ cm^3 g^{-1} or m^3 kg^{-1}

2.5.8 Units of molar refraction:

Since, $$R_m = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

The units of R_m are the same as of $\dfrac{M}{d}$

$$\frac{M}{d} = \frac{\text{g mol}^{-1}}{\text{g cm}^{-3}} = \text{cm}^3 \text{ mol}^{-1}$$

In SI units, $$\frac{M}{d} = \frac{\text{kg mol}^{-1}}{\text{kg m}^{-3}} = \text{m}^3 \text{ mol}^{-1}$$

Hence, the units of 'R' are m^3 mol^{-1} in SI, system. The values of refractive index, specific refraction and molar refraction of some important liquids at 20°C are provided in the following table (6).

Table (6) Refractive index, specific refraction and molar refraction of some important liquids at 20°C.

Compound	n_D^{20}	$[R_D]^{20}$	$[R_{m(D)}]^{20}$
Acetone	1.3588	0.2782×10^{-3}	1.615×10^{-5}
Benzene	1.5010	0.3354×10^{-3}	2.618×10^{-5}
Carbon tetrachloride	1.4600	0.1724×10^{-3}	2.651×10^{-5}
Chloroform	1.4455	0.1780×10^{-3}	2.125×10^{-5}
Ethanol	1.3613	0.2775×10^{-3}	1.278×10^{-5}
Toluene	1.4969	0.3356×10^{-3}	3.092×10^{-5}
Water	1.3328	0.2083×10^{-3}	0.375×10^{-5}

2.5.9 Molar refraction as additive property:

The molar refraction of a molecule is the sum of atomic refractions of its constituents atoms. The nature of the bonds may be single, double or triple. The type of the cyclic ring also contributes towards the total R_m value of a compound. The molar refraction of some important atoms and bonds for D-line of sodium are reported as in the table (7).

Table (7). Molar refraction in $cm^3 \ mol^{-1}$ for atoms, groups and bonds.

Carbon (C)	2.418	COOH group	7.227
Hydrogen (H)	1.100	OH group	1.518
Chlorine (Cl)	5.967	3-membered ring	0.710
Bromine (Br)	8.861	4-membered ring	0.480
Iodine (I)	13.900	6-membered ring	0 – 0.15
Double bond	1.733	O in OH group	1.525
Triple bond	2.398	O is C = O group	2.211
Methyl radical	5.653	O in ether	1.64
Ethyl radical	10.300		

EXAMPLE (7)

The refractive index of carbon tetrachloride at 20°C is 1.4573. Calculate its molar refraction, if its density is 1595 kg m^{-3}.

SOLUTION:

Data:

$$n = 1.4573, \quad d = 1595 \ kg \ m^{-3},$$
$$M = 154 \times 10^{-3} \ kg \ mol^{-1}, \quad R_m = \ ?$$

Using

$$R_m = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

Putting the values

$$R_m = \frac{(1.4573)^2 - 1}{(1.4573)^2 + 2} \times \frac{154 \times 10^{-3} \ kg \ mol^{-1}}{1595 \ kg \ m^{-3}}$$

$$= \frac{(2.12 - 1)}{(2.12 + 2)} \left(\frac{154 \times 10^{-3}}{1595} \right) \ m^3 \ mol^{-1}$$

$$R_m = \frac{1.12}{4.12} \times \frac{154 \times 10^{-3}}{1595} \ m^3 \ mol^{-1}$$

$$R_m = \frac{172.48 \times 10^{-3}}{6571.4} \ m^3 \ mol^{-1}$$
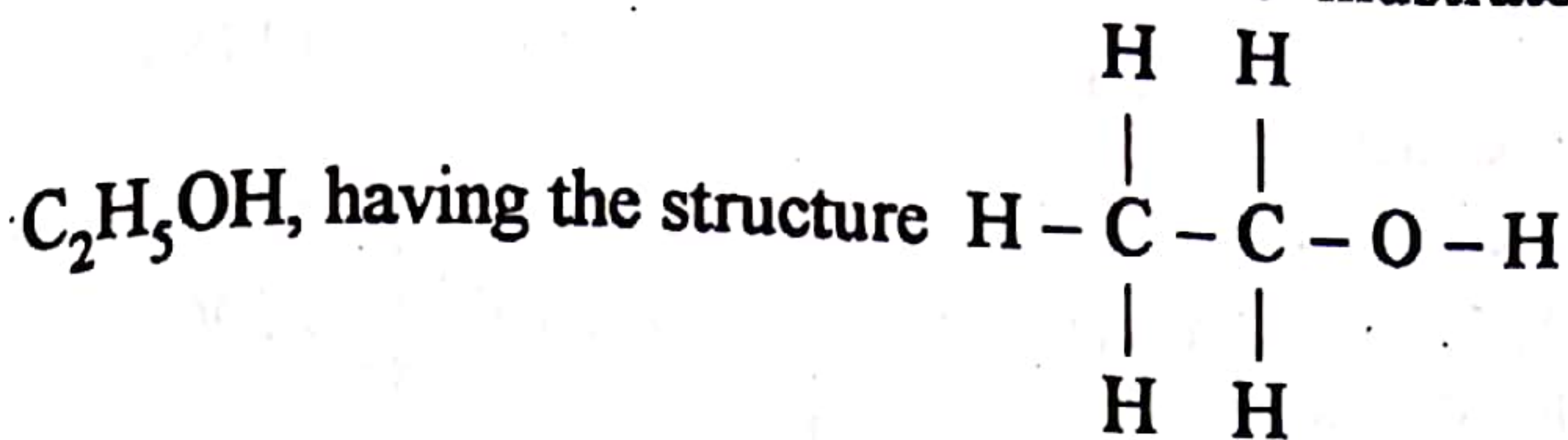
$$R_m = 0.0262 \times 10^{-3} \ m^3 \ mol^{-1}$$

$$R_m = \boxed{2.62 \times 10^{-5} \ m^3 \ mol^{-1}} \quad \text{Ans.}$$

2.5.10 Molar refraction and chemical constitution:

The molar refractions are calculated for various possible structures and the formula which is in accordance with the calculated molar refraction is the correct structure of that compound. In order to illustrate it, let us take the example of

C_2H_5OH, having the structure

$$H - \overset{\displaystyle \overset{H}{|}}{\underset{\displaystyle \underset{H}{|}}{C}} - \overset{\displaystyle \overset{H}{|}}{\underset{\displaystyle \underset{H}{|}}{C}} - O - H$$

Refractive index of C_2H_5OH = 1.3611

Density of C_2H_5OH = 0.7885 g cm^{-3}

Temperature of C_2H_5OH = 23°C

Source of light = sodium D-line

Molar mass of C_2H_5OH = 46 g mol^{-1}

$$R_m = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} = \frac{(1.3611)^2 - 1}{(1.3611)^2 + 2} \times \frac{46}{0.7885}$$

$$= \boxed{12.91 \text{ cm}^3 \text{ mol}^{-1}} \text{ Ans.}$$

Theoretical value of 'R_m' from the table is 12.916 cm^3 mol^{-1} or 1.2916 × 10^{-5} m^3 mol^{-1}. So, the correct structure of C_2H_5OH is as proposed above.

2.5.11 Molar refraction of the solution:

The molar refraction 'R_m' of the solution is given by the following relationship.

$$R_m = \frac{n^2 - 1}{n^2 + 2} \left(\frac{X_1M_1 + X_2M_2}{d} \right)$$

Where 'X_1' and 'X_2' are the mole fractions of the solvent and the solute. 'M_1' and 'M_2' are the molar masses of solvent and solute respectively.

2.5.12 Optical abnormality:

When the organic compounds having open chains have conjugated system of single and double bonds, then their experimental and theoretical 'R_m' values do not agree with each other.

Experimental 'R_m' value for such compounds is greater than the theoretical one. The difference of the two is called optical exaltation. When a carbonyl group is in conjugation with a double bond, then optical exaltation is also there.

The following table (8) shows the values of optical exaltation for some of the conjugated systems.

Table (8). Conjugated system showing optical exaltation.

S. No.	Formula	Name	Observed $[R_m]$	Calculated $[R_m]$	Optical exaltation
1	$CH_3 - CH = CH - CH = CH - CH_3$	2, 4 – Hexadiene	3.064×10^{-5}	2.889×10^{-5}	$+ 0.175 \times 10^{-5}$
2	$CH_2 = CH - CH = CH - CH = CH_2$	1, 3, 5 – Hexatriene	3.058×10^{-5}	2.852×10^{-5}	$+ 0.206 \times 10^{-5}$
3	$(CH_3)_2 C = CH - \overset{\overset{O}{\|}}{C} - CH = C(CH_3)_2$	Phorone	4.539×10^{-5}	4.273×10^{-5}	$+ 0.266 \times 10^{-5}$
4	$CH_2 = CH - (CH_2)_2 - CH = CH_2$	1, 5– Hexadiene	2.877×10^{-5}	2.889×10^{-5}	-0.012×10^{-5}

2.5.13 Optical exaltation and the benzene ring:

The conjugated system of double bonds present in a closed ring structure like benzene do not give optical exaltation. The experimental and theoretical R_m values of benzene are 2.618×10^{-5} and 2.630×10^{-5} m^3 mol^{-1}, respectively.

These values are very close to each other. Anyhow, the following organic compounds show optical abnormalities.

Acetophenone ,   Styrene ,   Napthalene ,   Anthracene
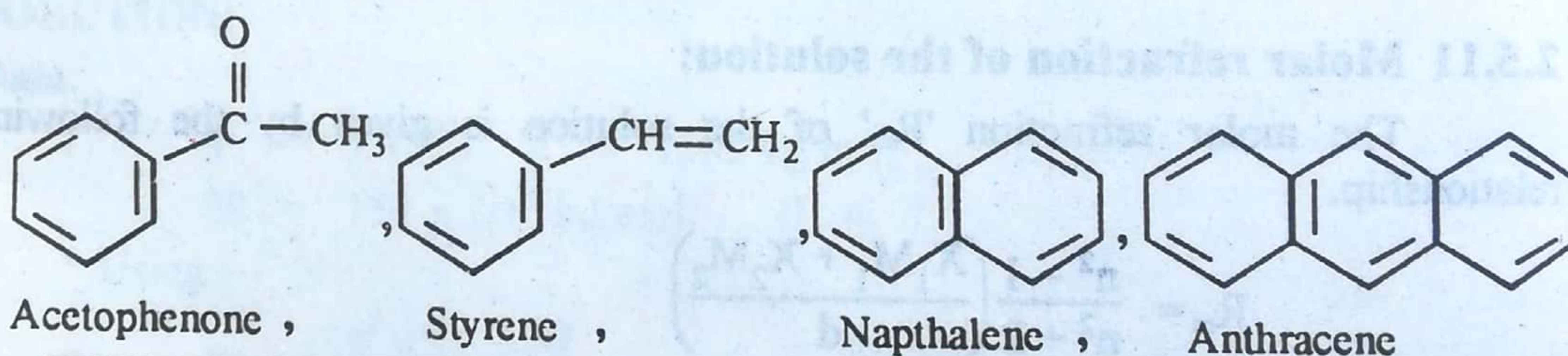
2.6.0 DIELECTRIC CONSTANT OF A MEDIUM

The idea of a dielectric constant of a substance can be best understand from the Coulomb's law. According to this law, the force of interaction between two fixed charges q_1^+ and q_2^- separated by distance 'r' is given by the following formula.

$$F = \frac{q_1 q_2}{\in r^2} \qquad \ldots\ldots (1)$$

$\in$ = Dielectric constant of the medium.

It gives us the measurement of the extent of decreasing force of attraction between the two charges q_1 and q_2.

For the vacuum, $\epsilon = 1$, so, Coulomb's law in the simplified form is as follows,

$$F = \frac{q_1 q_2}{r^2}$$

When the value of ϵ is greater, then the molecules which are interacting with each other due to charges q^+_1 and q^-_2 decrease their forces of attraction. The value of ϵ is 80 for water. It means that the charges q_1 and q_2 immersed in H_2O decrease the forces of attraction between them 80 times as compared to vacuum. The same two charges when immersed in acetone decrease the forces of attraction around 20 times. The values of dielectric constants for some liquids, at 25°C are given in the following table (9).

Table (9). Dielectric constants of some liquids at 25°C

Acetone	21.2	Diethyl ether	4.30
Benzene	2.28	Ethanol	24.3
Carbon tetrachloride	2.24	Hexane	1.90
Cyclohexane	2.03	Nitorbenzene	34.8
Chloroform	4.80	Water	78.5

2.6.1 Dielectric constant as constitutive property:

It is general observation that non-polar substances like benzene, carbontetrachloride, cyclohexane and hexane have low values of dielectric constants, while the liquids like acetone, water, alcohol and nitrobenzene have high values of dielectric constants. It means that dielectric constant depends upon the structure of the substances. For this reason, it is a constitutive property.

2.6.2 Measurement of dielectric constant:

Dielectric constant of substance is determined by the measurement of capacitance. The material whose dielectric constant is required is placed between the two plates of a capacitor and its capacitance is determined. It is denoted by C. Similarly, 'C' is determined, when there is vacuum between the plates of condenser.

$$\epsilon = \frac{C_{med}}{C_{vac}}$$

Mostly in place of vacuum, we take standard reference liquid say benzene, so,

$$\frac{\epsilon_1}{\epsilon_2} = \frac{C_1}{C_2}$$

ϵ_1 = Dielectric constant of the required liquid.

ϵ_2 = Dielectric constant of the standard liquid benzene.

C_1 = Capacitance of required liquid.

C_2 = Capacitance of the standard liquid.

The value of the ϵ can help us to estimate the polarity of a compound and so, we can calculate the dipole moment of a compound from it.

2.7.0 DIPOLE MOMENT

2.7.1 Introduction:

Those molecules in which the electron pair making the bonds are not equally shared are responsible for creating the dipole. This is due to difference of electronegativity between two atoms. Dipole moment is the property which is associated with such type of molecules.

Definition:

Dipole moment is the product of electrical charge and the distance between the two charges.

Mathematically,

$$\mu = d \times e$$

d = Distance between two charges

e = Charge on any one of the poles.

μ = Dipole moment.

Dipole moment is a vector quantity, so it is represented by an arrow. This arrow shows the direction from positive to the negative charge. The magnitude of the dipole moment is indicated by the length of arrow, as shown in the following diagram.

$$\mu = d \times e$$
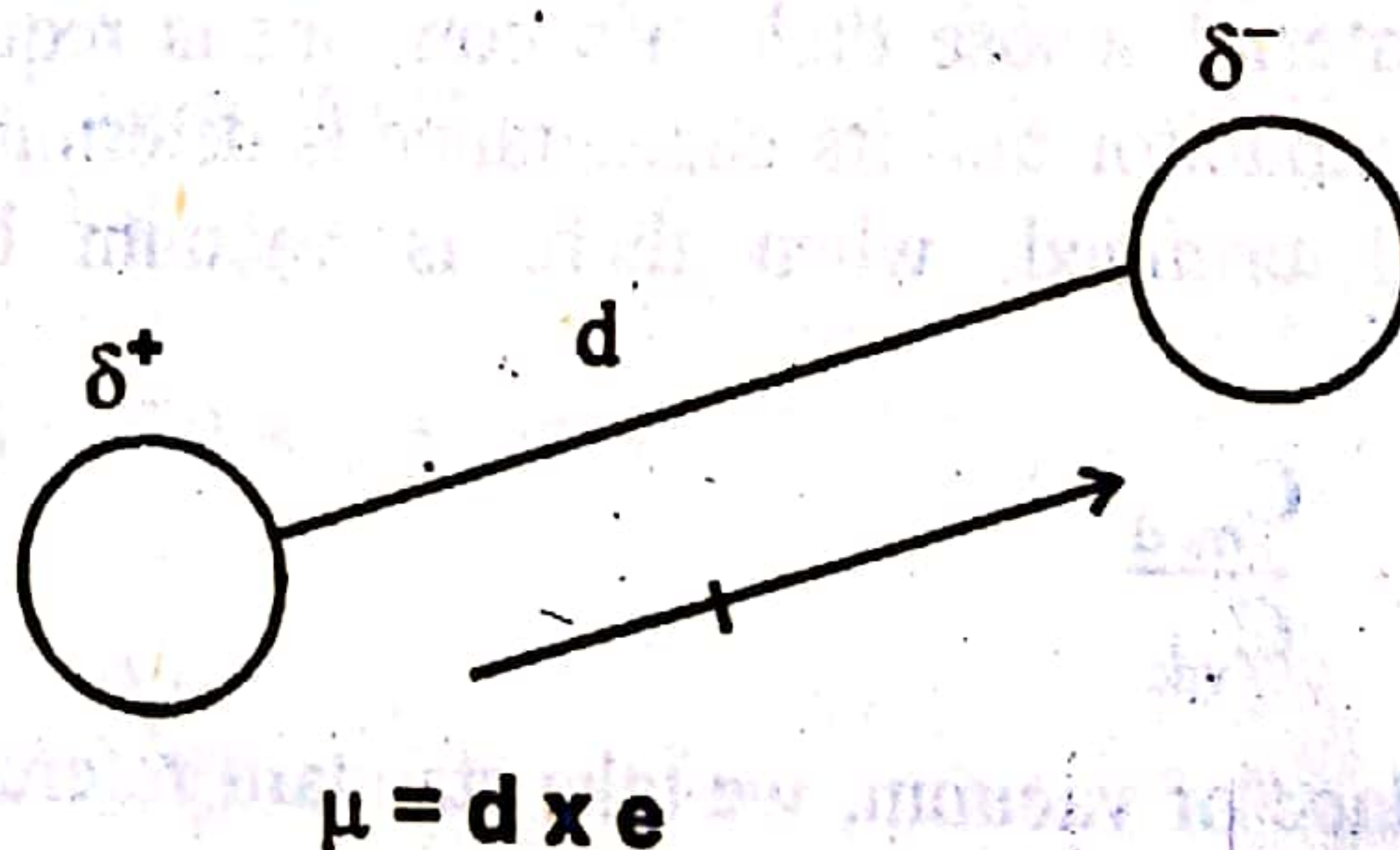
Dipole moment can help us to have the quantitative measurement of the extent to which a molecule is polar. It also helps to know the molecular configuration of the substance.
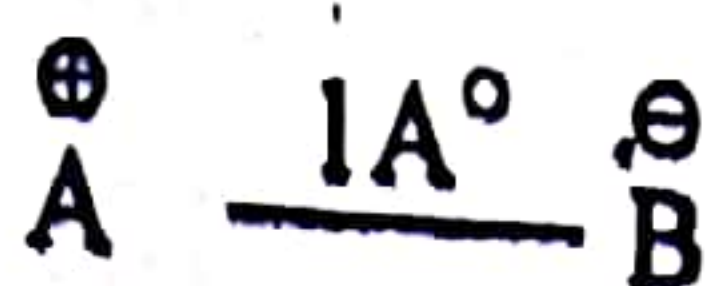
2.7.2 Units of dipole moment:

In order to derive the units, consider hypothetical molecule $A^\oplus - B^\ominus$, which has 100% ionic bond. In that case, 'A' has full positive and 'B' has full negative charge.

$$\overset{\oplus}{A} \xrightarrow{1A^\circ} \overset{\ominus}{B}$$

Suppose that the bond distance is $1A^\circ$.

Since, $\mu = d \times e$

$$d = 1A^\circ = 10^{-8} \text{ cm (in C.G.S. system)}$$

$$e = 4.8 \times 10^{-10} \text{ c. s. u (in C.G.S. system)}$$

$$\mu = 10^{-8} \text{ cm} \times 4.8 \times 10^{-10} \text{ E.S.U.} = 4.8 \times 10^{-18} \text{ cm e. s. u.}$$

$$10^{-18} \text{ cm c. s. u.} = 1 \text{ Debye} = 1D$$

Hence, $\mu = 4.8D$

So, Debye is the unit of dipole moment in C. G. S. system.

In SI system, the distance is taken in meters and charge in coulomb.

$$d = 1A^\circ = 10^{-10} \text{ m (in SI units)}$$

$$e = 1.602 \times 10^{-19} \text{ c (in SI units)}$$

$$\mu = 10^{-10} \text{ m} \times 1.602 \times 10^{-19} \text{ C} = 1.602 \times 10^{-29} \text{ mC}$$

$$\mu = 16.02 \times 10^{-30} \text{ mC}$$

In SI system, the unit of dipole moment is mc. Anyhow, the absolute values of both dipole moments are same for the same molecule $\overset{\oplus}{A} - \overset{\ominus}{B}$. (which is thought to be 100% ionic).

Hence, $4.8D = 16.02 \times 10^{-30} \text{ mC}$

$$1D = 3.338 \times 10^{-30} \text{ mC}$$

With the help of this relationship, we can interconvert two types of units of dipole moment.

2.7.3 Dipole moments of molecules:
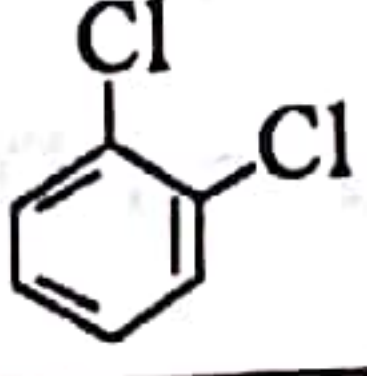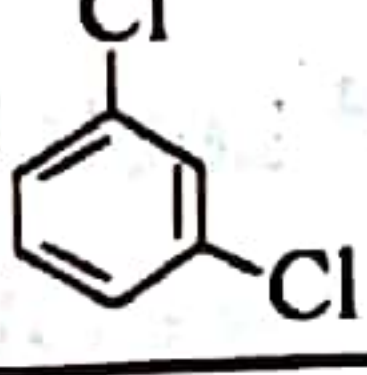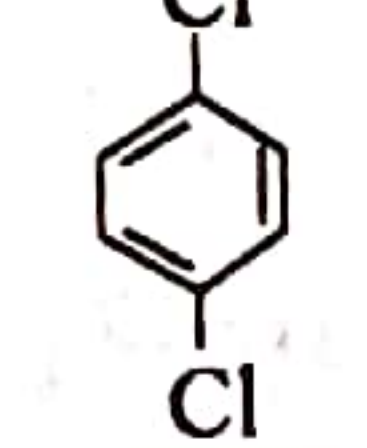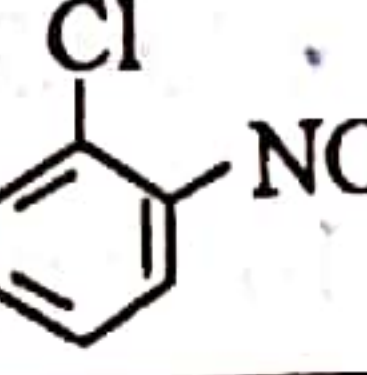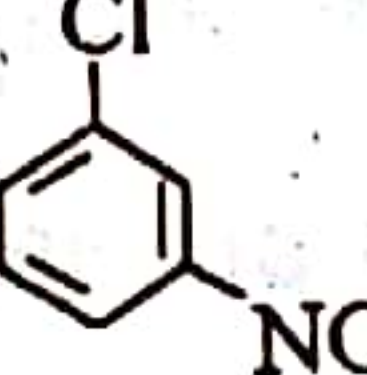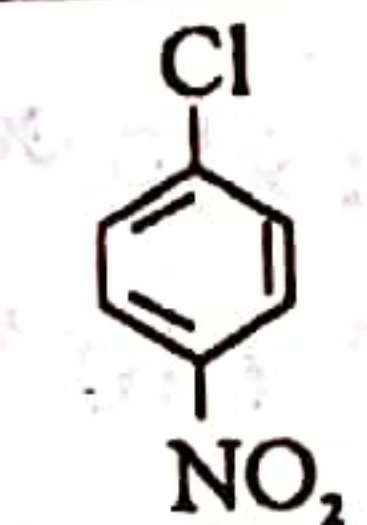
Diatomic molecules:

The homonuclear diatomic molecules like H_2, F_2, Cl_2, Br_2, I_2, O_2, N_2 etc. have zero dipole moments, because there is no charge separation. Heteronuclear diatomic molecules like HF, HCl, HBr, HI and CO have dipole moments. These values depend upon their bond lengths and electronegativity differences between the bonded atoms. The table (11) shows the values of dipole moments for such molecules.

μ - depend
— bond length
— E.N.

Table (11) Dipole moments of some important molecules in Debyes.

Molecule	μ	Molecule	μ
H_2	0	CH_3-I	1.35
HF	1.91	CH_2Cl_2	1.55
HCl	1.08	$CHCl_3$	1.15
HBr	0.80	C_2H_5-OH	1.70
HI	0.42	PCl_3	0.78
H_2O	1.85	$AsCl_3$	1.59
H_2S	1.10	N_2O	0.17
SO_2	1.61		2.50
HCN	2.23		1.72
CH_3NH_2	1.24		0
CH_3COOH	1.74		4.64
CH_3-Cl	1.87		3.73
CH_3-Br	1.45		2.83

Following compounds have zero dipole moments:

CS_2	0	CO_2	0
BF_3	0	C_2H_6	0
CH_4	0	C_2H_4	0
CCl_4	0	C_2H_2	0
C_2H_6	0	Cl_2	0

Polyatomic molecules:

In a polyatomic molecules every two bonded atoms have their dipole moments. This is called bond moment. Molecule of H_2O has two bond moments while that of NH_3 has three and CH_4 has four. The net dipole moment of a polyatomic molecule is the resultant of different bond moments. Value of the net dipole moment depends upon the direction of the bonds.

Consider triatomic molecules 'AB_2', having bond angle 'θ'. Let 'μ_{AB}' is the value of each bond moment Fig. (17). Then the dipole moment of the molecule will be

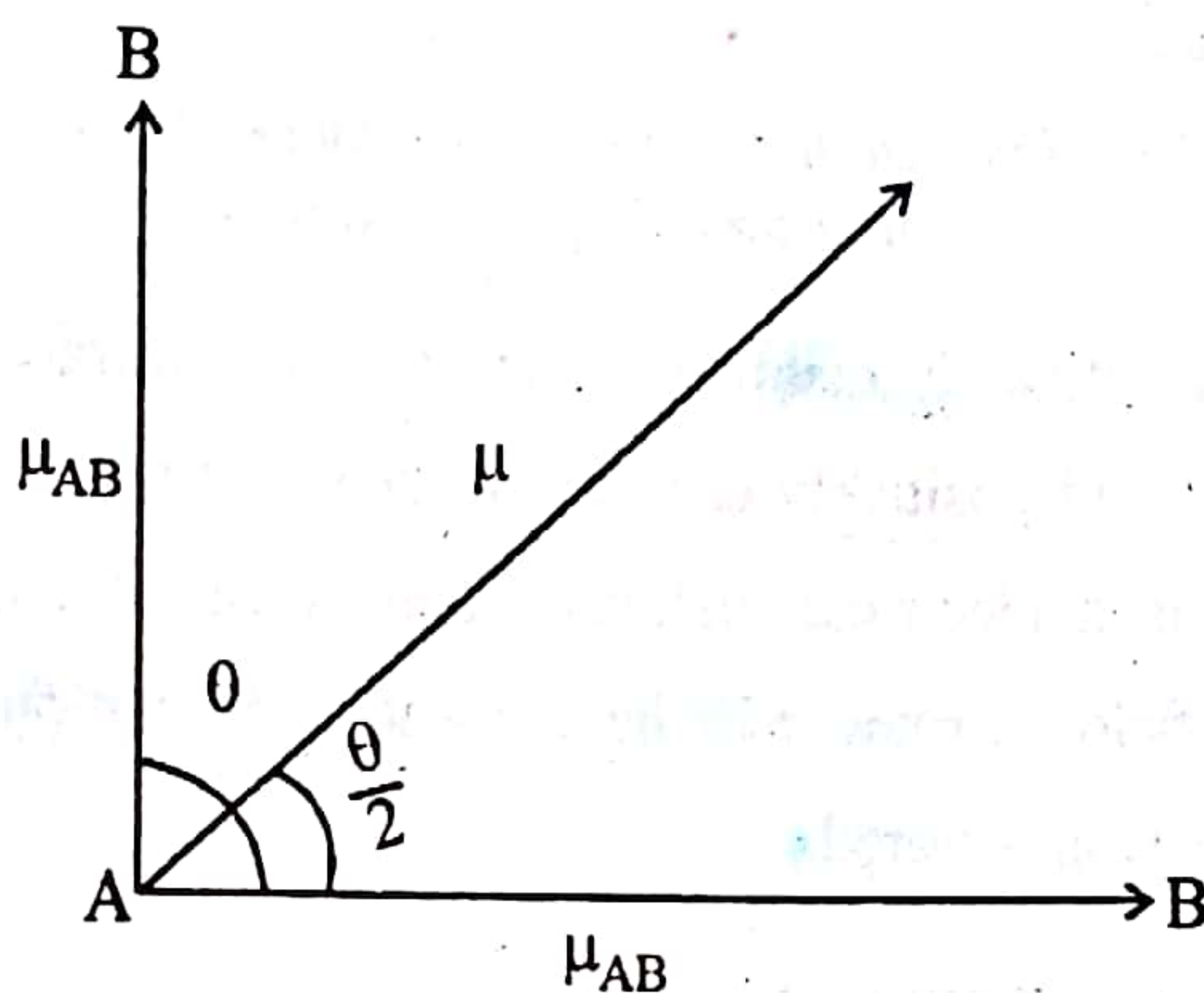$$\mu = 2\mu_{AB} \cos \frac{\theta}{2} \qquad \cdots\cdots (1)$$

Fig. (17) Net dipole moment of a triatomic molecule.

Greater the value of angle θ, between two bond moments, lesser the value of $\cos \frac{\theta}{2}$ and lesser the net dipole moment.

If we have a general molecule ABC, with two bonds as AB and AC and their bond moments are μ_1 and μ_2. Then dipole moment of the molecule will be,

$$\mu = \sqrt{\mu_1{}^2 + \mu_2{}^2 + 2\mu_1\mu_2 \cos \theta} \qquad \cdots\cdots (2)$$

This equation (2) is very useful in the sense that, if we know the value of angle 'θ' between the bonds and the experimental dipole moment 'μ', then we can calculate the bond moments μ_1 and μ_2. Anyhow, the same method can be used for calculating the angle 'θ' between the bonds.

2.7.4 Polarization of molecules:

The molecules are made up of positively charged nuclei and negatively charged electronic cloud. The center of the positive charge coincides with the center of the negative charge. When such a molecule is subjected to the action of an electrical field as shown in the following diagram (18), then polarization is developed.
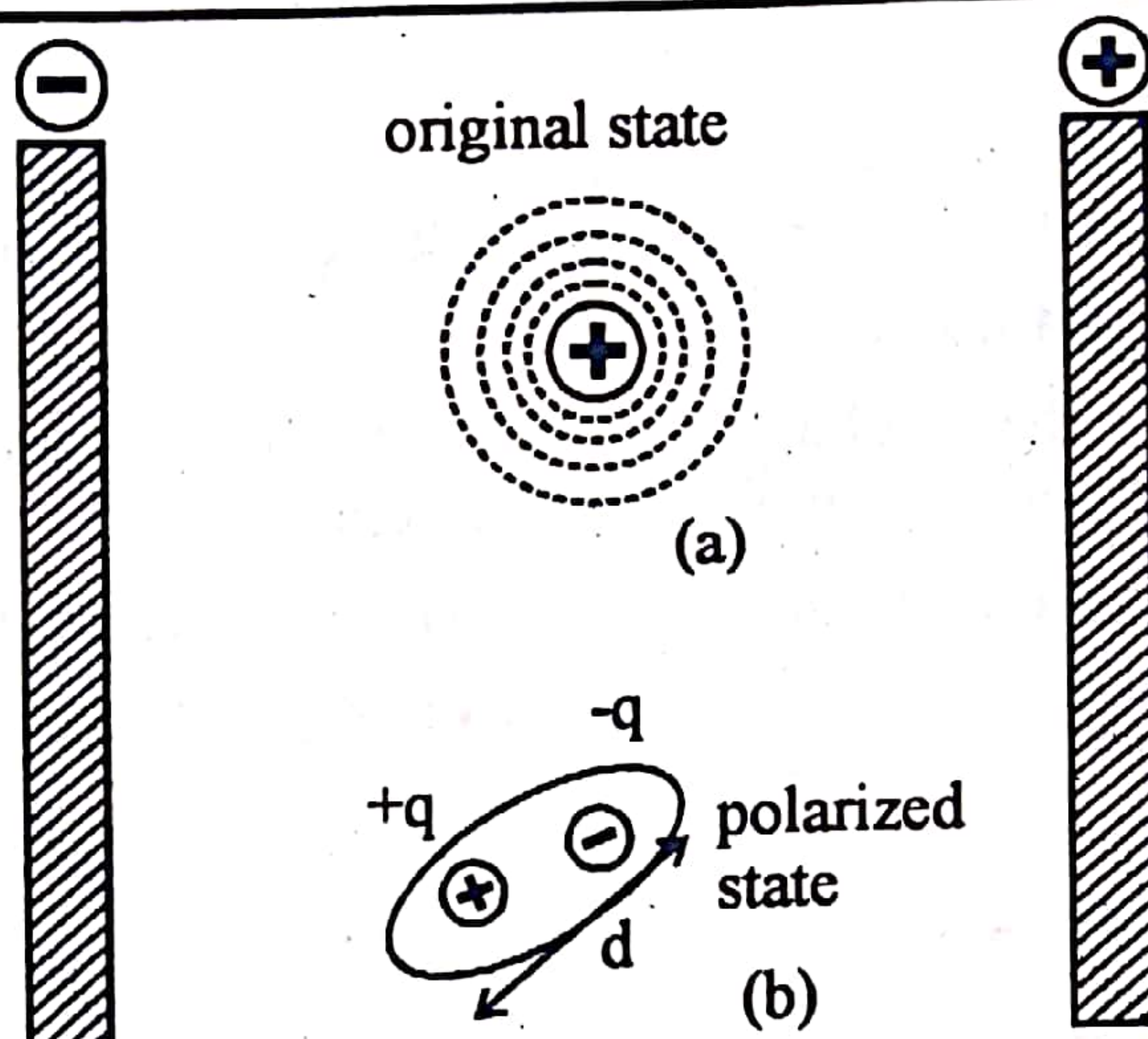
Fig. (18) Polarization of a molecule by electric field
(a) original state (b) polarized state.

The electronic cloud is disturbed. Electrons are attracted by the positive plate of the condenser and positively charged portion of a molecules is attracted by negative plate. This is a electrical distortion and is called induced polarization. When the electrical field is removed, the induced polarization disappears and a symmetrical distribution is restored.

2.7.5 Induced dipole moment:

The degree of induced polarization depends upon the strength of electric field and the nature of the molecule. This thing is independent of temperature. Hence,

$$\mu_i = \propto \times X \qquad \cdots\cdots (3)$$

μ_i = Induced dipole moment
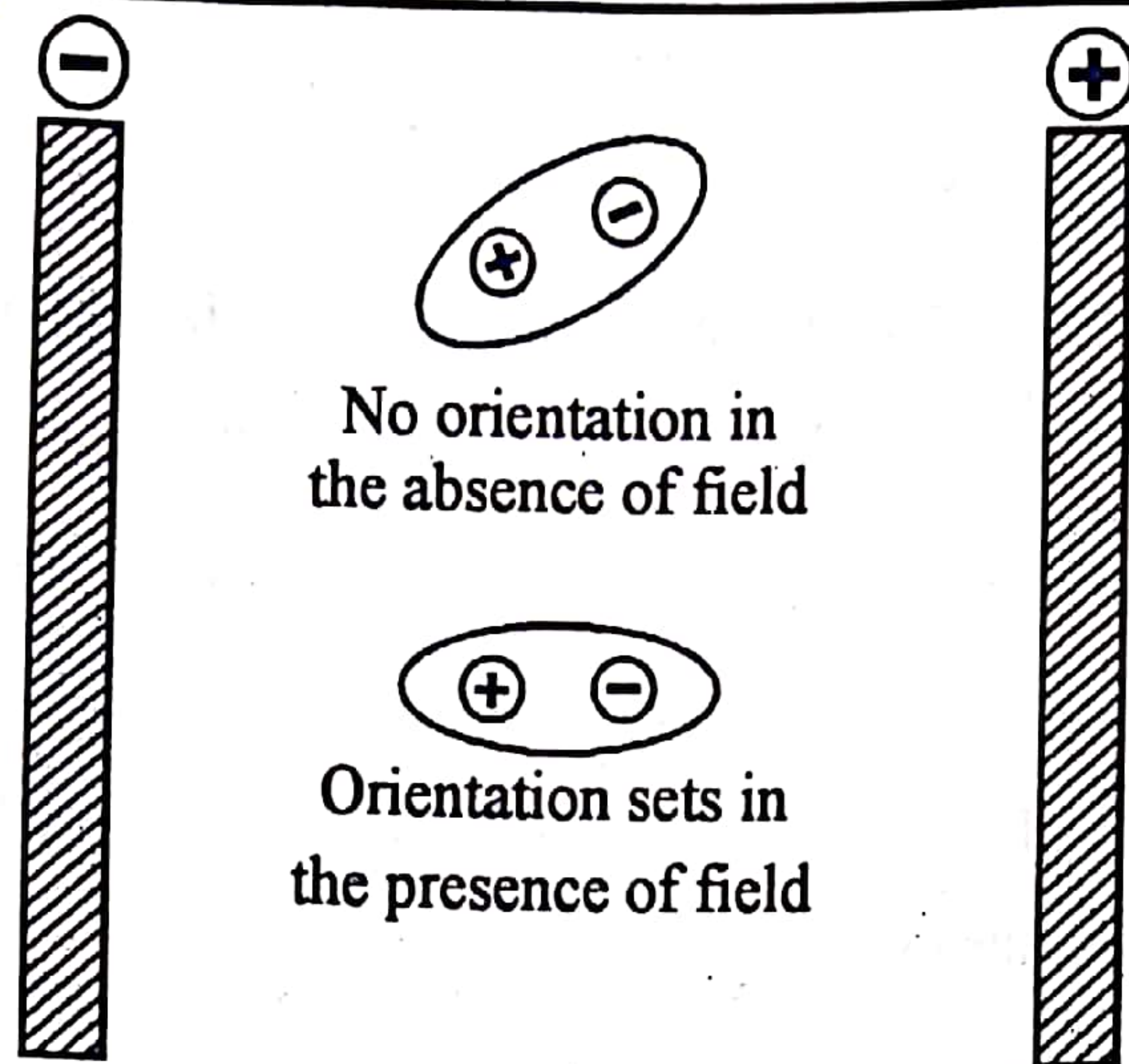
$\propto$ = Polarizability of the molecule

X = Strength of electrical field.

2.7.6 Orientation polarization:

If the molecule is polar, like HCl, HBr, HI, then temporary moment is induced in them and the polar molecules also tend to become orientated parallel to one another, as shown in the following diagram (19).

(handwritten margin notes top-left: "→ Thermal agitation", "→ K.E possess", "α →", "Orientation ↳ Temp. dependent")

Fig. (19) Orientation of polar molecules in electrical field.

(handwritten margin notes right: "Permanent dipole ↳ orientation induced")

Anyhow, due to thermal agitation and possession of kinetic energy, the molecules feel resistance to get the proper orientation. This is called orientation polarization and it is temperature dependent. Orientation polarization will decrease with the increase of temperature. The temperature affects the behaviour of the substance in an electric field is used to make a distinction between the polar and non-polar substances.

(handwritten margin note right: "Non-polar → induced orientation")

2.7.7 Mathematical treatment of total polarization:

If the molecule is non-polar like H_2, Cl_2, Br_2 etc., then only induced polarization is there first of all and then orientation is developed. In the case of molecules having permanent dipoles, there is orientation polarization first of all and then induced polarization.

It means that the total polarization is definitely present in every type of molecule.

(handwritten margin note right: "Polar. Induced & Orientation } Non-polar Polar")

$$P_m = P_i + P_o \qquad \cdots\cdots (4)$$

P_m = Total molar polarization

P_i = Induced polarization

P_o = Orientation polarization

The total polarization is related to dielectric constant of the medium, molar mass of the substance and the density of the substance by the following equation.

$$P_m = \frac{\epsilon - 1}{\epsilon + 2}\left(\frac{M}{d}\right) \qquad \cdots\cdots (5)$$

This equation (5) is called Clausius-Mossottii equation. Combining equation (4) and (5)

$$P_m = P_i + P_o = \frac{\epsilon - 1}{\epsilon + 2}\left(\frac{M}{d}\right) \qquad \cdots\cdots (6)$$

According to equation (6), the sum of induced and orientation polarization can be calculated from the dielectric constant of the substance, molar mass and density of the substance.

2.7.8 Formulas of induced and orientation polarizations:

Debye has given the following expression for P_i and P_o.

$$P_i = \frac{4}{3} \pi N_A \alpha \qquad \cdots\cdots (7)$$

$$P_o = \frac{4}{9} \frac{\pi N_A \mu^2}{kT} \qquad \cdots\cdots (8)$$

N_A = Avogadro's number

α = Polarizationality of the substance

μ = Dipole moment

k = Boltzmann constant

T = Temperature

The orientation polarization is inversely proportional to temperature and directly proportional to the square of the dipole moment. Clausius-Mossottii equation can be written as,

$$P_m = \frac{(\epsilon - 1)}{(\epsilon + 2)} \frac{M}{d} = \frac{4}{3} \pi N_A \alpha + \frac{4}{9} \frac{\pi N_A \mu^2}{kT} \qquad \cdots\cdots (9)$$

2.7.9 Relationship of refractive index:

According to Maxwell's electromagnetic theory of light $\epsilon = n^2$, where 'n' is the refractive index of the substance.

Anyhow, the Maxwell's relation is only valid, when

(i) the substance has no permanent dipole

(ii) longer wavelength is used for the radiations

(iii) refractive index is not measured in the regions of wavelength where the radiation is absorbed.

We know that the molar refraction has the following expression.

$$R_m = \frac{(n^2 - 1)}{(n^2 + 2)} \frac{M}{d}$$

In this situation, this is corresponding to 'Pi' i.e., induced polarization.

Hence, $P_i = R_m = \frac{(n^2 - 1)}{(n^2 + 2)} \frac{M}{d} = \frac{4}{3} \pi N_A \alpha \qquad \cdots\cdots (10)$

It means that according to Maxwell's relation,

$$R_m = P_m = P_i$$

The value of 'R_m' is measured from the refractive index of the liquid and solid and expression for total molar polarization is

$$P_m = \frac{(\epsilon - 1)}{(\epsilon + 2)} \frac{M}{d} = R_m + \frac{4}{9} \frac{\pi N_A \mu^2}{kT} \qquad \ldots\ldots (11)$$

According to equation (11) the dipole moment of a substance can be calculated, if we know the dielectric constant, molar mass, density and refractive index of the substance.

EXAMPLE (8)

The refractive index of benzene at 25°C for light of wavelength 600 nm is 1.498. The density of benzene is 0.874×10^3 kg m^{-3}. Calculate the molar polarization (p_m) and polarizability (α) of benzene.

$$M = 78.1 \times 10^{-3} \text{ kg mol}^{-1}$$

SOLUTION:

Data:

The molar mass of benzene is 78.1×10^{-3} kg.mol^{-1}

$$n = 1.498, d = 0.874 \times 10^3 \text{ kg m}^{-3},$$

Since,

$$[R_m] = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

Putting values,

$$R_m = \frac{(1.498)^2 - 1}{(1.498)^2 + 2} \times \frac{78.1 \times 10^{-3} \text{ kg mol}^{-1}}{0.874 \times 10^3 \text{ kg m}^{-3}}$$

$$= \frac{2.24 - 1}{2.24 + 2} \left(\frac{78.1 \times 10^{-3}}{0.874 \times 10^{+3}}\right) \text{ m}^3 \text{ mol}^{-1}$$

$$R_m = P_m = \frac{1.24}{4.24} \times \frac{78.1 \times 10^{-3}}{0.874 \times 10^{+3}} \text{ m}^3 \text{ mol}^{-1}$$

$$R_m = P_m = \frac{96.844 \times 10^{-3}}{3.705 \times 10^{+3}} \text{ m}^3 \text{ mol}^{-1}$$

$$R_m = P_m = 26.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

Since,

$$P_m = \frac{4}{3} \pi N_A \alpha$$

So,

$$\alpha = \frac{3 P_m}{4\pi N_A}$$

Putting values,

$$\alpha = \frac{3 P_m}{4\pi N_A} = \frac{3 \times 26.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}}{4 \times 3.143 \times 6.02 \times 10^{23} \text{ mol}^{-1}}$$

$$= \boxed{10.038 \times 10^{-30} \text{ m}^3} \text{ Ans.}$$

EXAMPLE (9) -

A known hydrocarbon has refractive index of 1.427 and density is 778.4 kg m^{-3}. Calculate its molar polarization and polarizability. The molar mass of cyclohexane is 84.16 g mol^{-1}.

SOLUTION:

Data:

$$n = 1.427$$

$$d = 778.4 \text{ kg m}^{-3}$$

$$M = 84.16 \text{ g mol}^{-1} = 84.16 \times 10^{-3} \text{ kg mol}^{-1}$$

$$\alpha = ?$$

Since

$$P_m = R_m = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{M}{d}$$

Putting values

$$P_m = \frac{(1.427)^2 - 1}{(1.427)^2 + 2} \times \frac{84.16 \times 10^{-3} \text{ kg mol}^{-1}}{778.4 \text{ kg m}^{-3}}$$

$$P_m = \frac{2.036 - 1}{2.036 + 2} \cdot \left(\frac{84.16 \times 10^{-3}}{778.4}\right) \text{ m}^3 \text{ mol}^{-1}$$

$$P_m = \frac{1.036}{4.036} \times \left(\frac{84.16 \times 10^{-3}}{778.4}\right) \text{ m}^3 \text{ mol}^{-1}$$

$$P_m = \frac{87.189}{3141.62} \times 10^{-3} = 0.02775 \ 10^{-3}$$

$$P_m = \boxed{2.775 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}} \quad \text{Ans.}$$

The formula for polarizability and P_m is as follows,

$$P_m = \frac{4\pi}{3} N_A \alpha$$

or $\quad \alpha = \dfrac{3P_m}{4\pi N_A}$

Putting the values,

$$\alpha = \frac{3P_m}{4\pi N_A} = \frac{3 \times 2.775 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}{4 \times 3.143 \times 6.023 \times 10^{23} \text{ mol}^{-1}}$$

$$\alpha = \boxed{1.099 \times 10^{-29} \text{ m}^3} \quad \text{Ans.}$$

2.7.10 Measurement of dipole moment:

There are two methods for the measurement of dipole moment.

(i) Vapour temperature method

(ii) Refraction method

(i) Vapour Temperature Method:

The substance whose dipole moment is required is converted into the vapour state. In the gaseous or vapour state, the molecules are far apart from each other. They do not induce electrical fields in the neighboring molecules. So, 'α' and 'μ', remain constant during the measurements.

Temperature of the vapours of the substance is changed and total molar polarization 'P$_m$' is measured. A graph is plotted between $\frac{1}{T}$ on x-axis and 'P$_m$' on y-axis. According to the following equation,

$$P_m = \frac{4}{9}\frac{\pi N_A \mu^2}{kT} + \frac{4}{3}\pi N_A \alpha = \frac{4}{9}\frac{\pi N_A \mu^2}{k}\left(\frac{1}{T}\right) + \frac{4}{3}\pi N_A \alpha \quad \cdots (9)$$

The graph should be straight line with positive slope. The value of the slope of a straight line should correspond to

$$\text{Slope} = \frac{4}{9}\frac{\pi N_A \mu^2}{k}$$

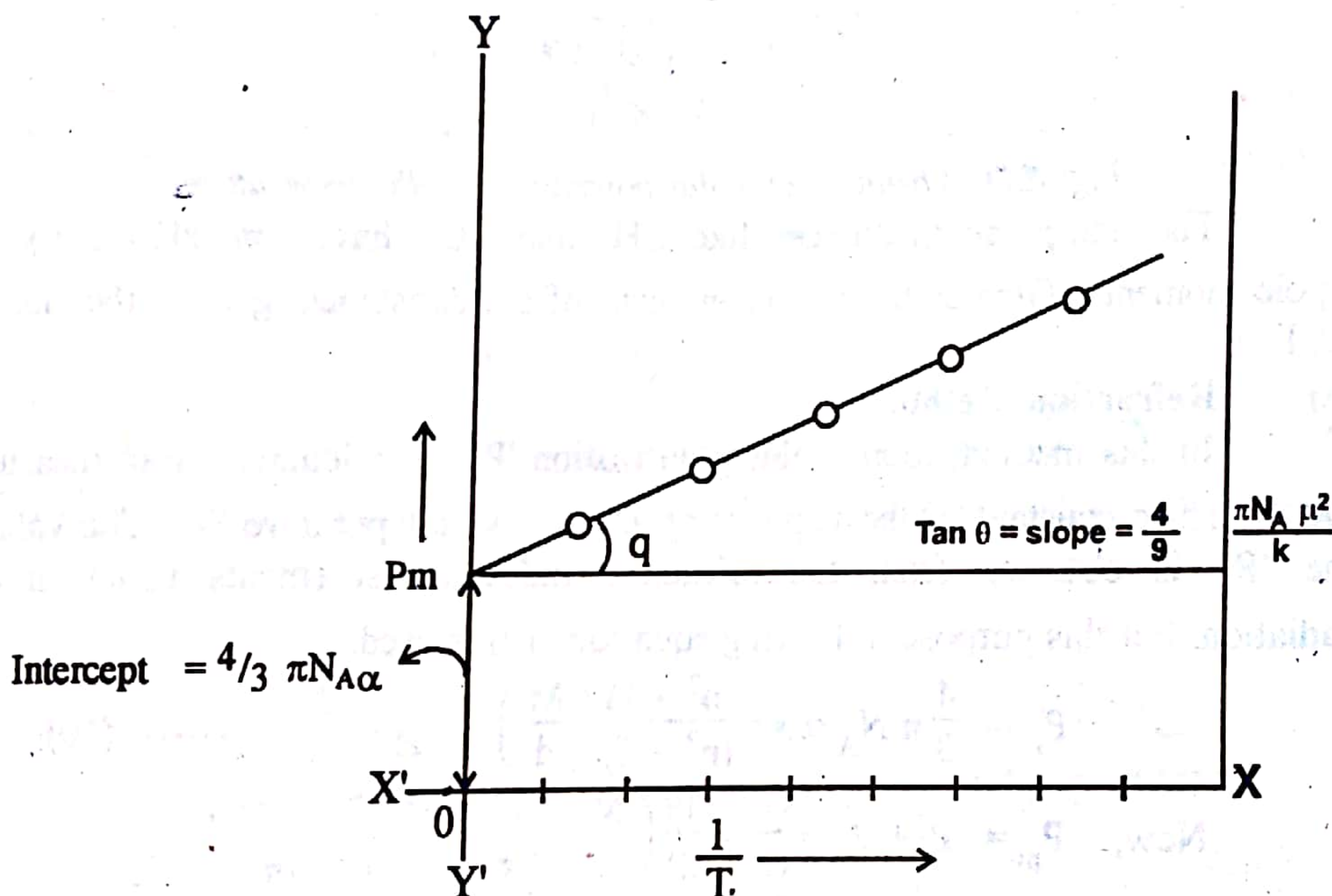and intercept of the straight line should be $\frac{4\pi}{3} N_A \alpha$. The graph is as under Fig. (20)

Fig. (20) Graph of $\frac{1}{T}$ vs P$_m$, to measure dipole moment by
vapour-temperature method.

$$\text{Slope} = \frac{4}{9}\frac{\pi N_A \mu^2}{k}$$

So, $\mu^2 = 9k\dfrac{\text{slope}}{4\pi N_A}$

or $\mu = \sqrt{\dfrac{9k}{4\pi N_A}} \cdot \sqrt{\text{slope}}$

Putting the values of constants like k, π, N_A, alongwith the units,

$$\mu = 0.0128 \times 10^{-18} \text{ cm e.s.u } \sqrt{slope}$$

Since, 10^{-18} cm. e.s.u $= 1D$

So, $\mu = 0.0128D \sqrt{slope}$ ...... (12)

This is the final equation for all the substances whose slopes can be measured and dipole moments can be calculated.

The graphical explanation of some of the substances are shown in the following diagram (21).
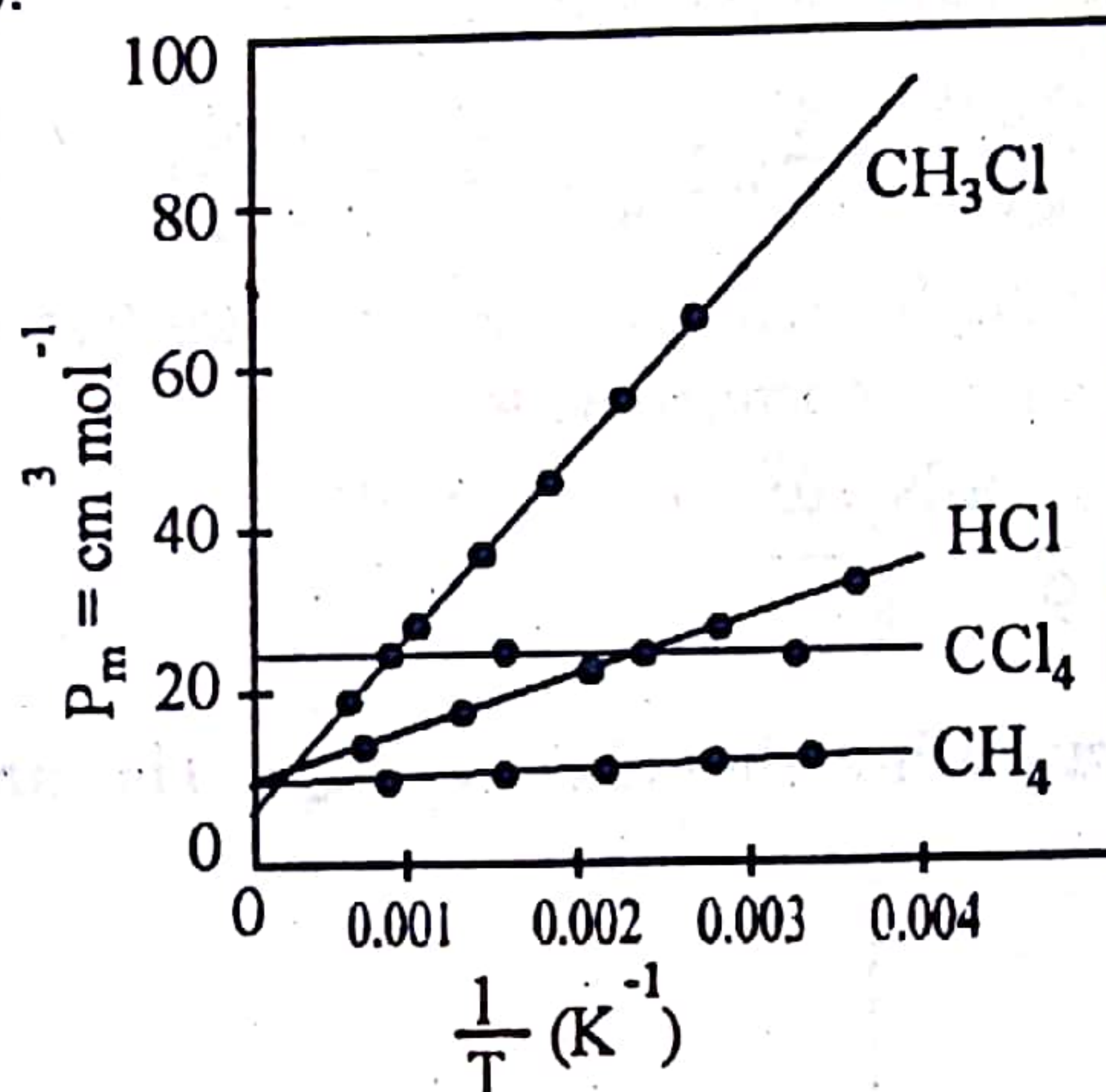

Fig. (21). Variation of molar polarization with temperature.

The non-polar substances like CH_4 and CCl_4 have zero slopes, so zero dipole moments. Greater the dipole moment of the substance, greater the slope of the line.

(ii)   **Refraction Method:**

In this method, total molar polarization 'P_m' is calculated from measuring the dielectric constant of the vapours at any known temperature 'T'. The value of the 'P_i' is obtained from the refractive index measurements using infrared radiation. For this purpose, following equation (10) is used.

$$P_i = \frac{4}{3} \pi N_A \alpha = \frac{(n^2 - 1)}{(n^2 + 2)}\left(\frac{M}{d}\right) \qquad \text{...... (10)}$$

Now, $P_m = P_i + P_o = \frac{(\epsilon - 1)}{(\epsilon + 2)}\left(\frac{M}{d}\right)$

$$P_o = \frac{4}{9} \frac{\pi N_A \mu^2}{kT}$$

$$P_m = P_i + \frac{4 \pi N_A \mu^2}{9 \ kT}$$

$$\mu^2 = (P_m - P_i)\frac{9kT}{4\pi N_A} \qquad \text{...... (13)}$$

Putting the value of constants as k, π and N_A in equation (13)

$$\mu = 0.0128 \sqrt{(P_m - P_i)T} \ D \qquad \text{...... (14)}$$

2.7.11 Applications of dipole moment measurements:

Dipole moment is one of the excellent constitutive property for liquids and solids. A few important applications are mentioned.

(i) Comparison of relative polarities:

The greater the electronegativity difference between two bonded atoms, greater the polarities and greater the values of dipole moments. The μ-values decrease from HCl to HI for halogen acids, because their polarities go on decreasing down the group.

(ii) Percentage of ionic character:

The polar covalent compounds are not 100 %.covalent. They have certain % age of ionic character in them. This can be calculated by the following formula.

$$\text{\%age ionic character} = \frac{\text{observed dipole moment}}{\text{diple moment of 100\% ionic bond}} \times 100$$
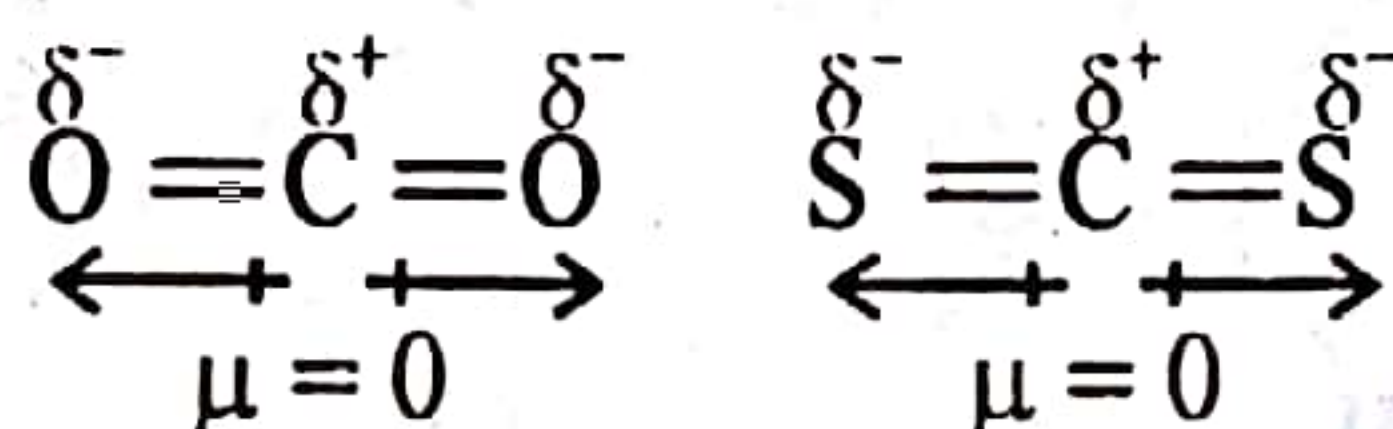
The dipole moment of 100% ionic character is calculated from the actual bond length and the charge of electron or proton.

(iii) Shape of molecules:

Dipole moment is vector quantity. Every bond in a compound has almost a constant value of bond moment. The net values of the bond moments give us information about the shapes of the molecules.

(a) Triatomic molecules:

Linear triatomic molecules like CO_2 and CS_2 have zero dipole moments because their bond moments cancel the effect of each other.

$$\overset{\delta^-}{O} = \overset{\delta^+}{C} = \overset{\delta^-}{O} \qquad \overset{\delta^-}{S} = \overset{\delta^+}{C} = \overset{\delta^-}{S}$$
$$\mu = 0 \qquad\qquad \mu = 0$$

Triatomic non-linear molecules like H_2O, H_2S and SO_2 etc. have net dipole moments as shown by the following diagram. They are bent molecules and are V-shaped.

net μ = 1.85D   net μ = 1.1D   net μ = 1.61D
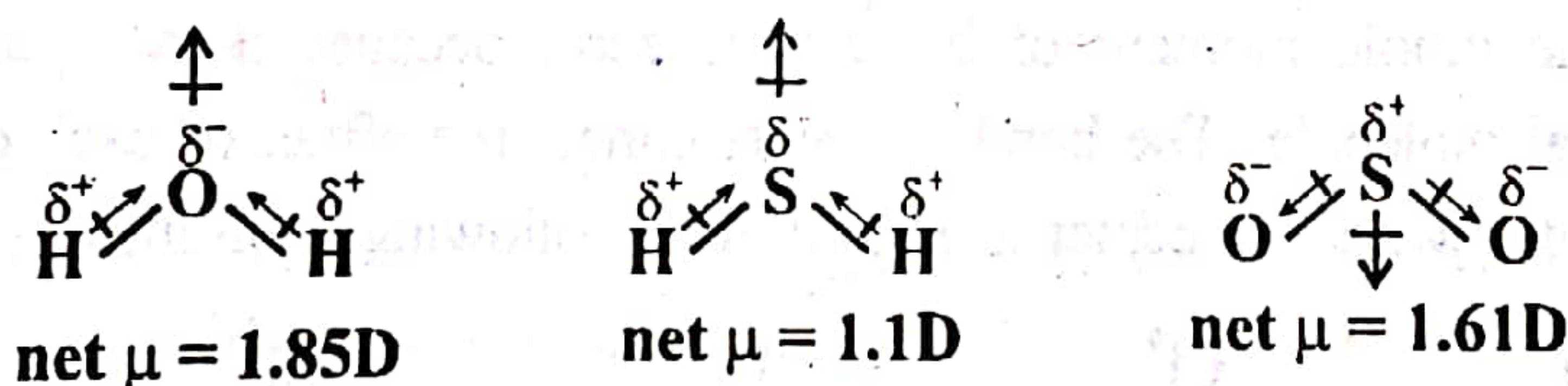
(b) Tetratomic molecules:

The molecules like BF_3, AlF_3 etc. are planar triangular and have zero μ values. Anyhow, the compounds like $\ddot{N}H_3$, $\ddot{N}F_3$, $\ddot{P}Cl_3$, $\ddot{P}F_3$ etc. have net dipole moments as shown in the following diagram. They are pyramidal in shape.

μ = 0   net μ = 1.47D   net μ = 0.75 D
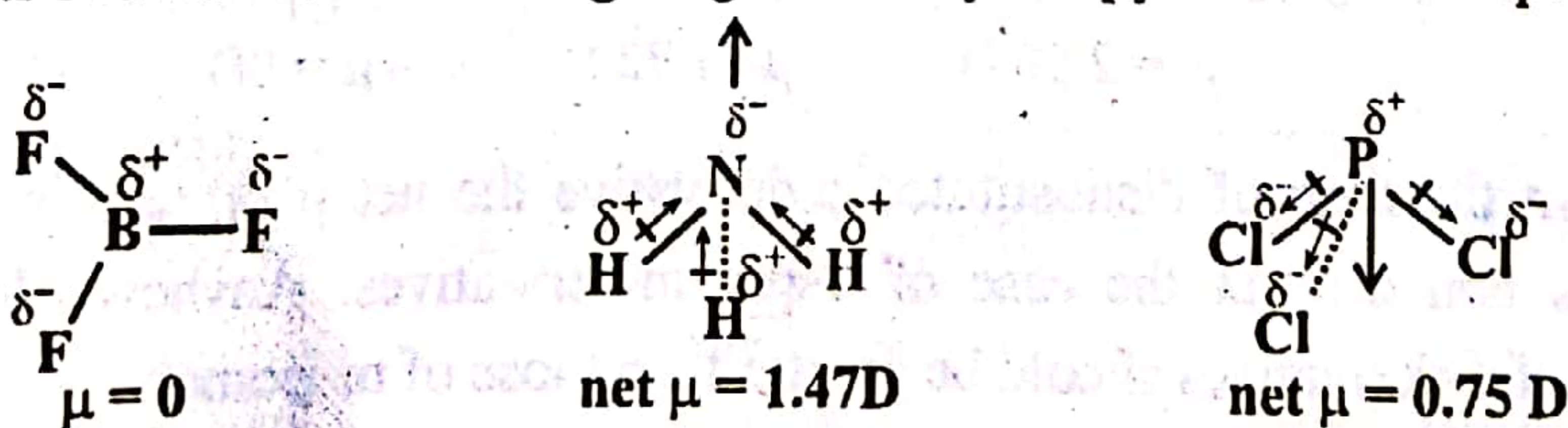
(c)   **Pentatomic molecules:**

Pentatomic molecules having symmetrical structure like CH_4, SiH_4, CCl_4 etc. have net dipole moments zero, because they are perfectly tetrahedral molecules as shown below. Anyhow, if one of the atoms attached with the central atom is substituted then the dipole moment is developed and its value depends upon the nature and size of group.

net $\mu = 0$ D   net $\mu = 1.78$ D
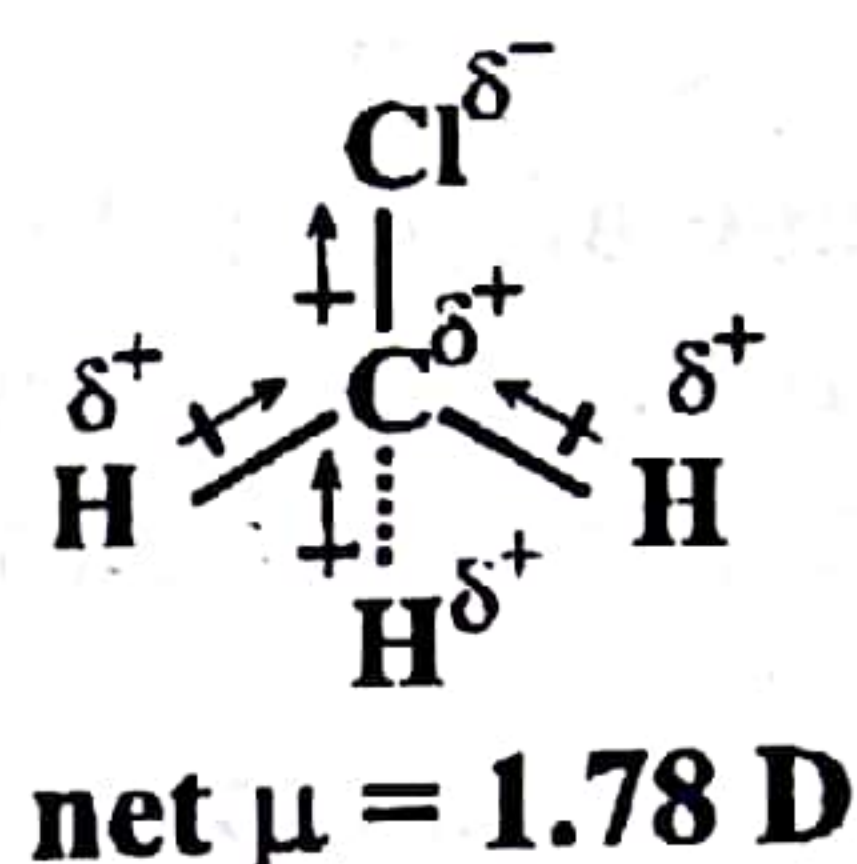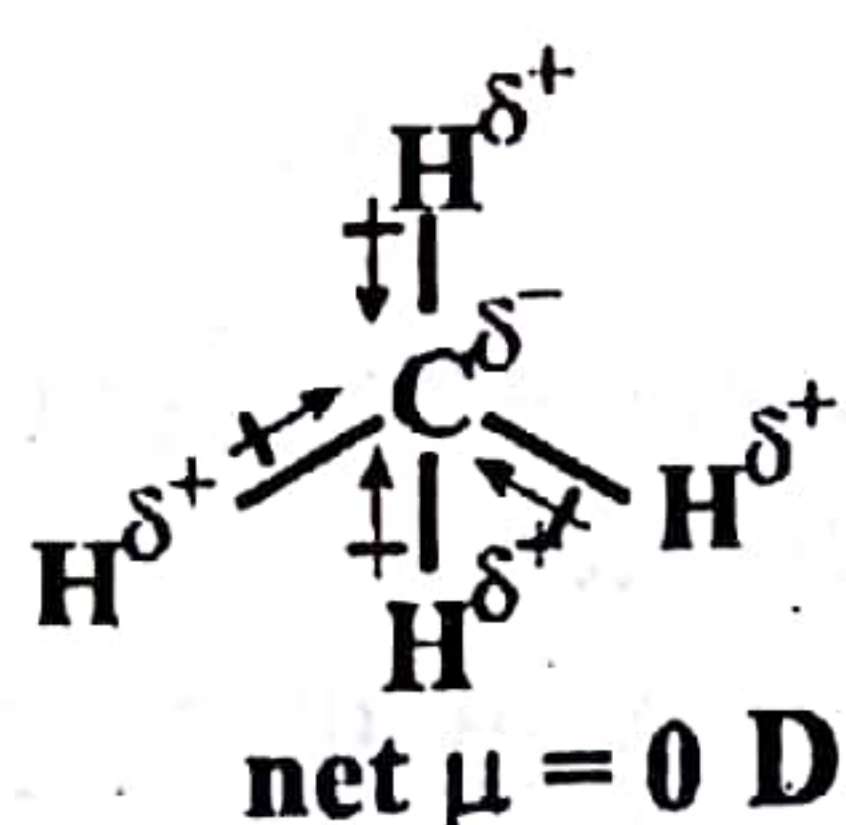
**(iv)**   **Comparison of cis and trans-geometrical isomers:**

Due to restricted rotation of the double bond or cyclic structure of a compound geometrical isomers are developed. In case of cis isomer, there is a certain value of dipole moment but the bond moments cancel the effect of each other in trans-isomer.

Following diagram makes the idea clear.

net $\mu \neq 0$D   net $\mu = 0\bar{D}$
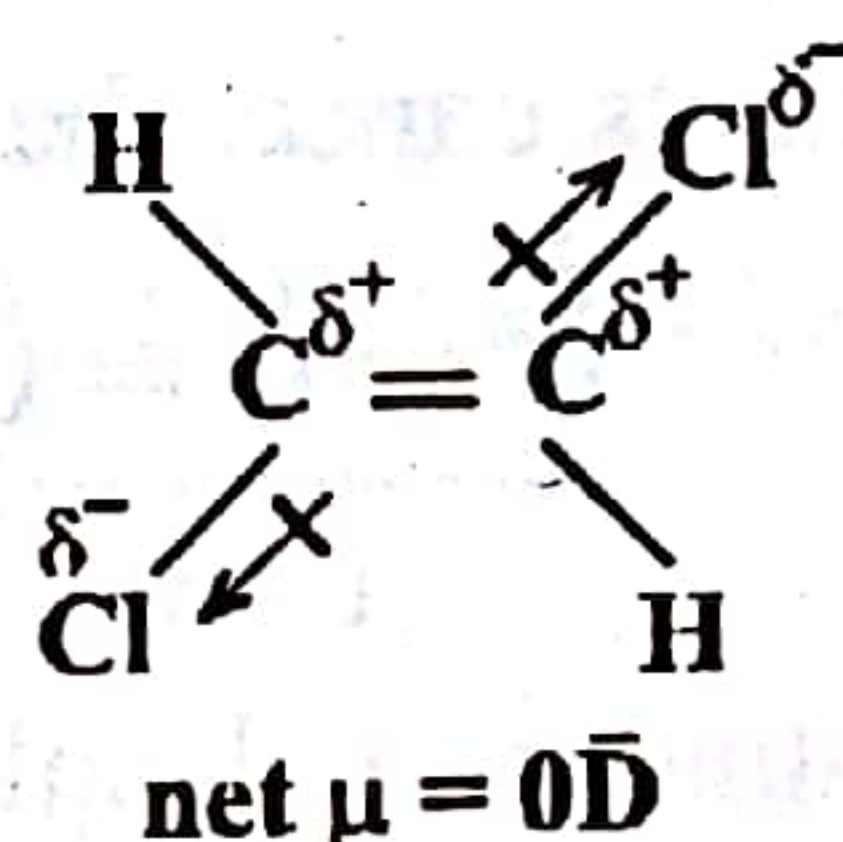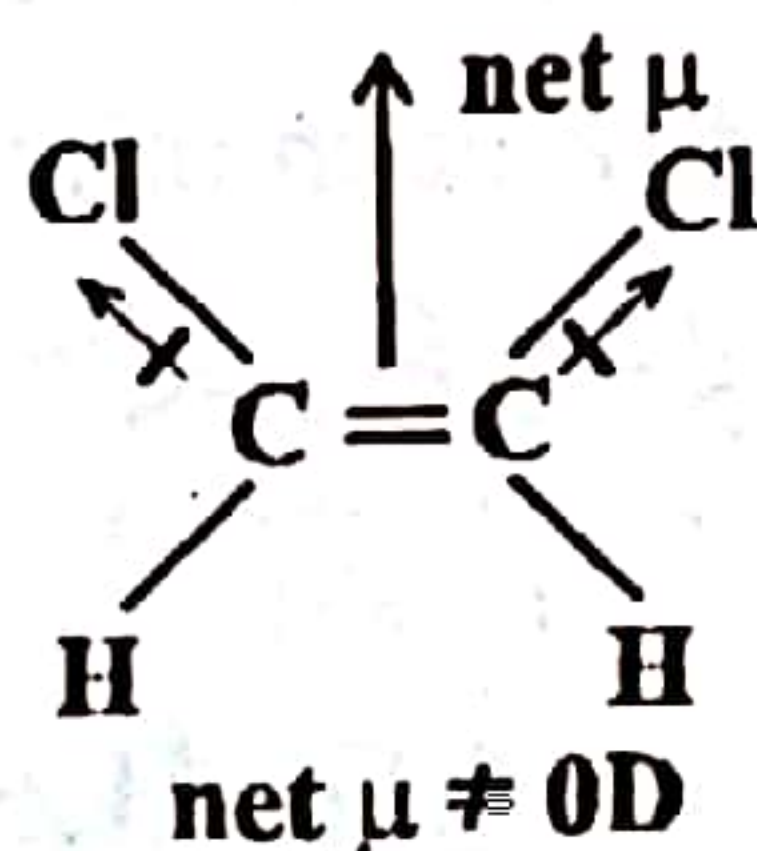
(v)   **Comparison of o, m, p-isomers:**

The dipole moment of benzene is zero, because it is regular hexagonal symmetrical molecule. The bond moments cancel the effect of each other and they are directed towards the center as shown in the following diagram.

$\mu = 2.50$ D μ - 1.72 D $\mu = 0$D
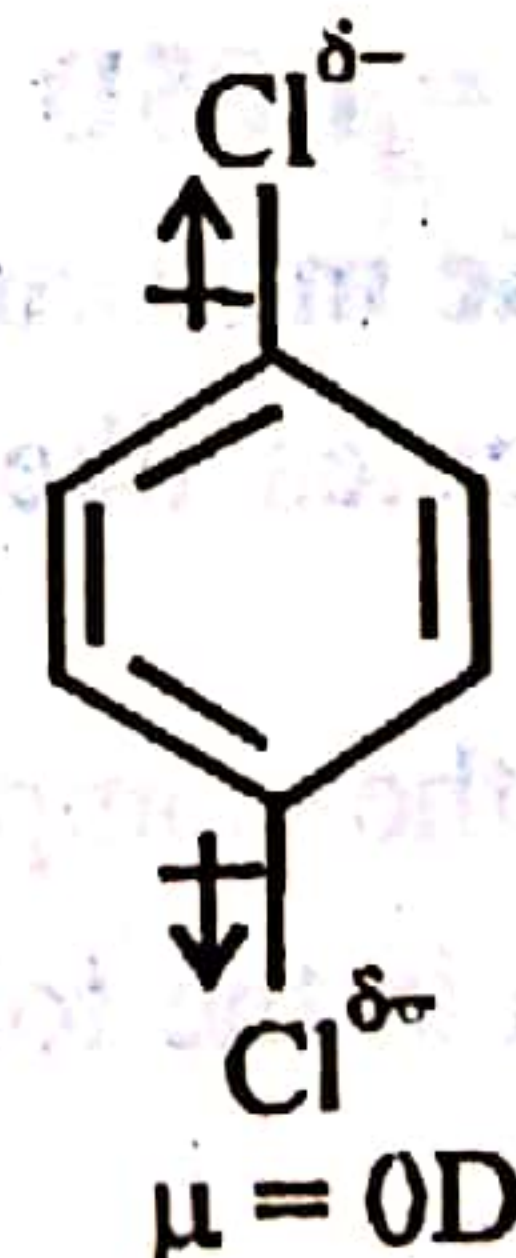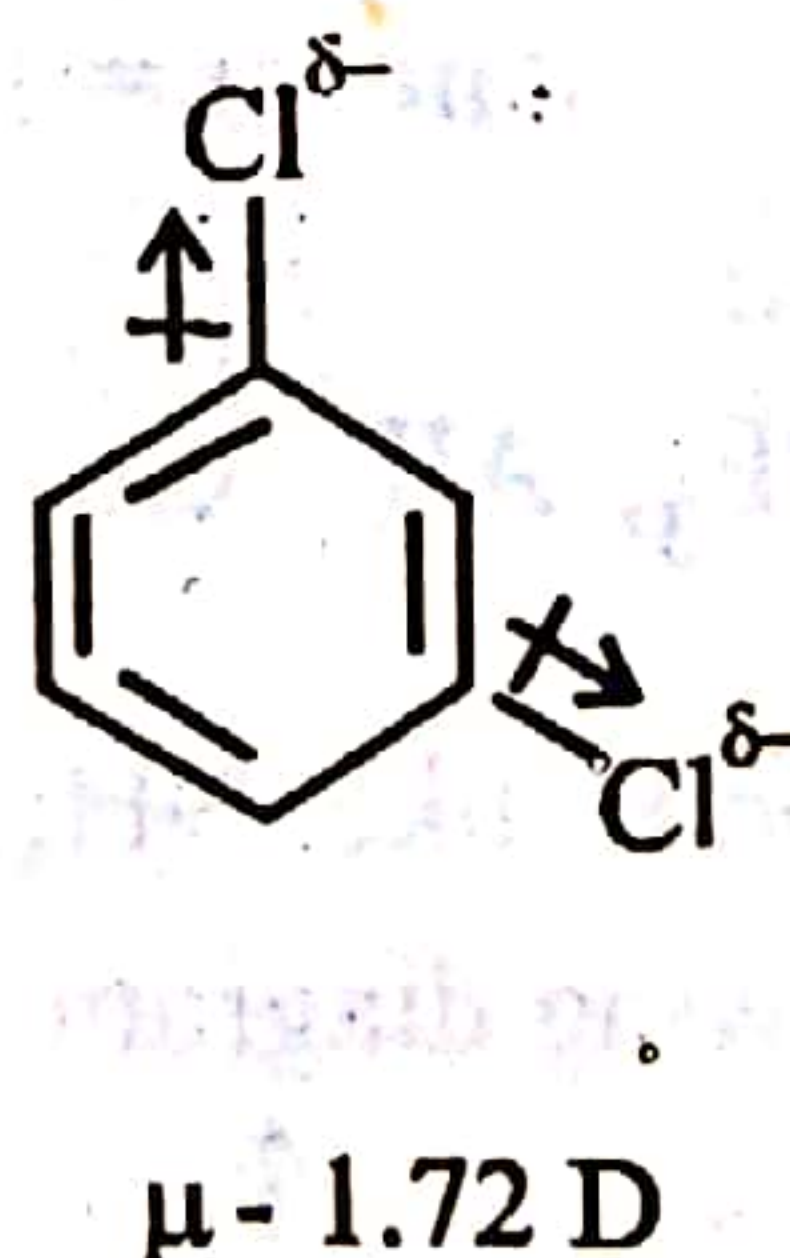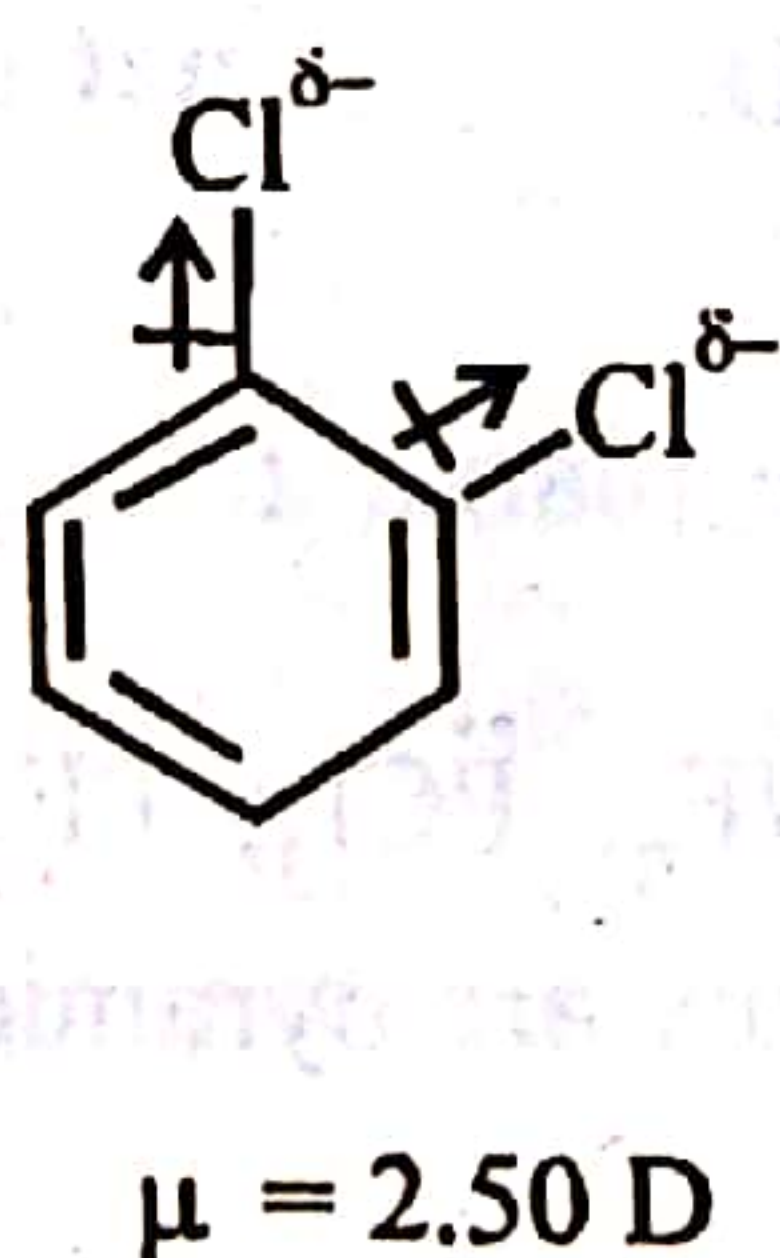
In the case of disubstituted p-derivative the net μ is zero in many cares. But it is non zero in the case of o-and m-derivatives. Anyhow, the net dipole moment of o-derivatives should be greater than those of m-isomers.

2.8.0 MAGNETIC PROPERTIES

2.8.1 Introduction:

It is a common observation that some of the substances feel interaction with the magnetic field. i.e., they are attracted or repelled by the magnetic field. We have to look at the reasons for these properties and the measurement of magnetic susceptibility.

2.8.2 Magnetic permeability:

"Magnetic permeability is the tendency of magnetic lines of forces to pass through the medium as compared to that in the vacuum." To have an understanding of this factor, consider two magnetic poles of strength s_1 and s_2 which are separated by distance 'R'. Then the force acting between them is given by the following formula.

$$F = \frac{1}{\alpha} \frac{s_1 s_2}{R^2} \qquad \ldots\ldots (1)$$

"The parameter 'α' is the magnetic permeability of the medium between the two poles s_1 and s_2." There are three situations.

   (i) $\alpha = 1$ for vacuum or air.

   (ii) $\alpha < 1$ for diamagnetic substances.

   (iii) $\alpha > 1$ for paramagnetic substances.

2.8.3 Diamagnetic substances:

"When the magnetic lines of forces prefer to pass through the vacuum rather than through the substance comprising the medium then the medium is diamagnetic." Permeability. 'α' is less than unity in this case. Following diagram (28) makes the idea clear.

2.8.4 Paramagnetic substances:

"When the magnetic lines of forces have greater tendency to pass through the substance rather than through the vacuum, then that substance is paramagnetic in nature." It means that magnetic lines of forces are attracted towards the substances Fig. (22).

2.8.5 Ferromagnetic substances:

"Those substances which are paramagnetic in nature but their 'α' value is very high i.e. in the range of 10^3, then the substance is called ferromagnetic." Following diagram (22) makes the idea clear.

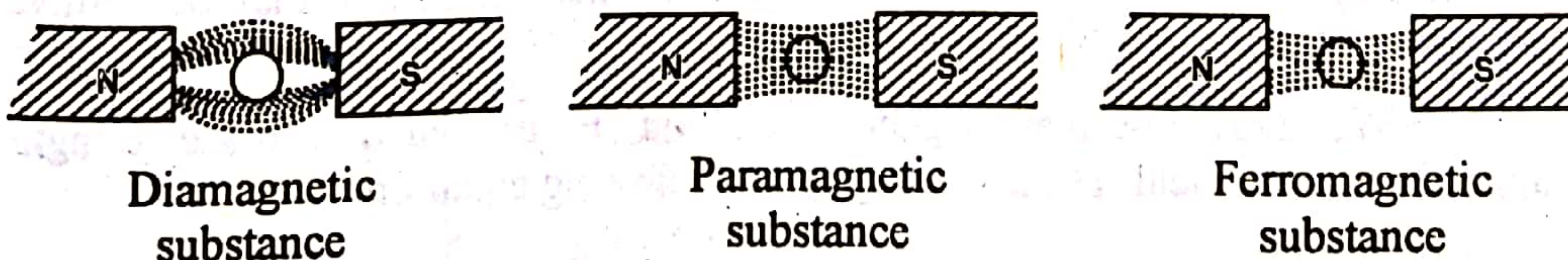| Diamagnetic substance | Paramagnetic substance | Ferromagnetic substance |

Fig. (22). Magnetic properties of substances.

2.8.6 Magnetic induction:

When material is placed in the magnetic field then the strength of the magnetic field in the material is different from that in vacuum. *"This strength of magnetic field present in the material is called magnetic induction."* Let us represented it by B. A relationship between strength of the applied magnetic field 'H' and the magnetic induction 'B' is as follow,

$$B = H + 4\pi I \qquad \cdots\cdots (1)$$

I = Magnetic moment per unit volume or intensity of magnetization.

'I' may be positive or negative. I is positive for paramagnetic substances and negative for diamagnetic substances.

2.8.7 Specific magnetic susceptibility:

"It is the ratio of intensity of magnetization 'I' and the applied magnetic field strength 'H'". In other words, we can say that it is the intensity of magnetization produced per unit strength of applied magnetic field. It mostly denoted by χ (chi)

$$\chi = \frac{I}{H} \qquad \cdots\cdots (2)$$

If we want to study the magnetic properties of different materials, then χ is measured experimentally.

Units of Measurement

$$\chi = \frac{I}{H} = \frac{\text{Mag. moment / vol.}}{\text{Mag. field}}$$

$$= \frac{\text{Bohr Magneton}}{\text{cm}^2 \text{ ocrsted}} = \text{B.M. cm}^{-2} \text{ os}^{-1}$$

2.8.8 Molar magnetic susceptibility:

If we multiply $\frac{I}{H}$ with molar volume i.e. $\frac{M}{d}$ of the material then we get the magnetic susceptibility per mole. This is also called molar magnetic susceptibility. It is denoted by χ_m.

$$\chi_m = \frac{I}{H} \times \frac{M}{d} \qquad \cdots\cdots (3)$$

Definition:

"Molar magnetic susceptibility χ_m is the intensity of magnetization induced per mole of material per unit field strength." Remember that 'I' may be positive or negative.

We also know that magnetic induction 'B' is related with the strength of applied magnetic field 'H', according to the following equation.

$$B = \alpha H \qquad \cdots\cdots (4)$$

According to equation (2)

$$I = \chi H \qquad \qquad \dots\dots (5)$$

Let us put these values of 'B' and 'I' in equation (1).

$$\alpha H = H + 4\pi \chi H$$

$$\alpha = 1 + 4\pi \chi \qquad \qquad \dots\dots (6)$$

It means that according to equation (6) the magnetic permeability (α) is related with specific magnetic susceptibility 'χ' and it clears the idea about the nature of α.

'χ' may be positive or negative depending upon the nature of 'I'. It means that 'α' may be greater or lesser than unity. When 'χ' is zero then 'α' is unity which is true for vacuum.

2.8.9 Measurement of magnetic susceptibility:

Gouy's method for the measurement of magnetic susceptibility is one of the best methods. An electromagnetic is arranged as shown in the following diagram (23). The substance whose susceptibility is to be measured is taken in the tube 'T'. This tube is suspended vertically with a wire from one arm of the balance between two poles of an electromagnetic. The lower end of this tube should be in the middle of the pole. Weights are put in the pans of the balance to adjust the position of substance in the tube.
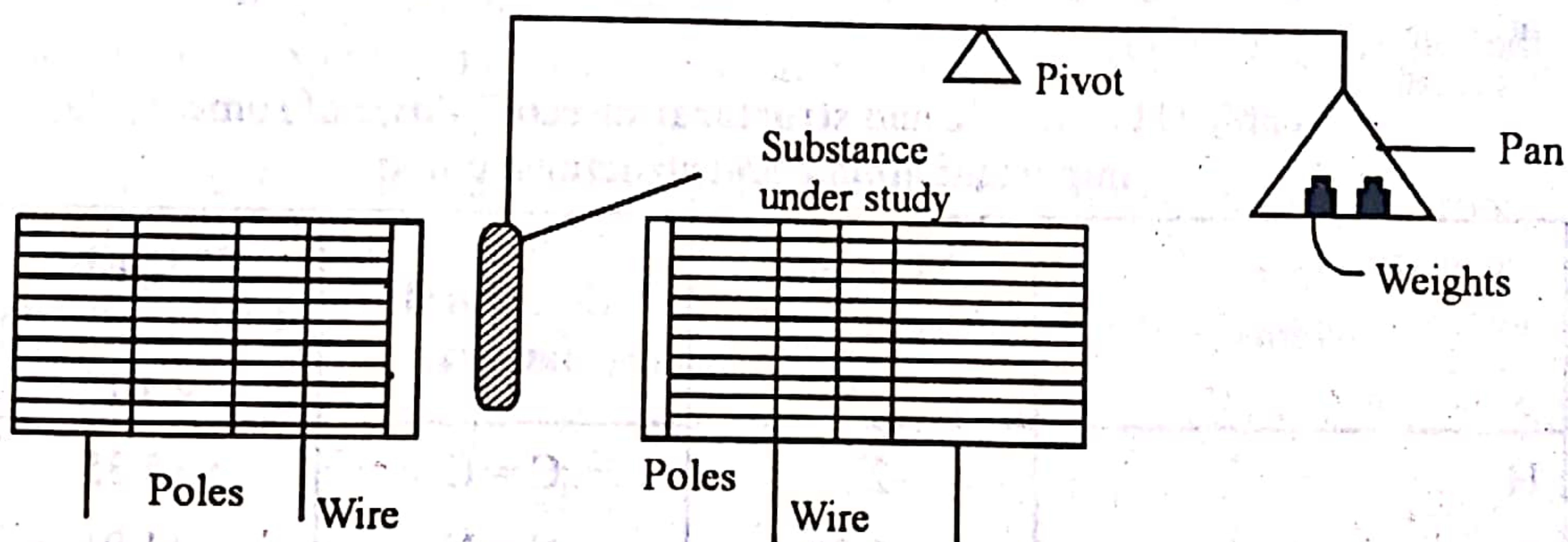

Fig. (23). Gouy's method for measurement of magnetic susceptibility.

Current is switched on into the electromagnetic. The tube is pulled down, when the substance is paramagnetic. So, some extra weights have to be added in the pan. If the substances in the tube is diamagnetic, then the tube is pushed upward, so, some weights have to be removed from the pan to maintain the original position of the balance.

Mathematical treatment:

Actually the change in the weight is equal to the magnetic force, acting on the material. Let the change in mass is Δm and its weight is Δmg. This weight depends upon the magnetic susceptibility, magnetic field strength and area of the contact of the specimen 'A'.

$$\Delta mg = \frac{1}{2}(\chi - \chi_a) AH^2 \qquad \qquad \dots\dots (7)$$

'χ_a' is volume susceptibility of air and its value is 0.03×10^{-6}. Using the equation (7) 'χ' can be calculated.

We can eliminate the factor 'A' and 'H' from the equation (7) by performing the experiment twice. The first experiment is performed with the substance of known susceptibility using the same magnetic field and the cylinder. Mostly water is taken as reference standard. If we apply equation(7) on both substances with same 'A', 'H' and 'g' values and dividing the two equations, we get the following expression.

$$\frac{\Delta m}{\Delta m_w} = \frac{\chi - \chi_a}{\chi_w - \chi_a} \qquad \cdots\cdots \text{ (8)}$$

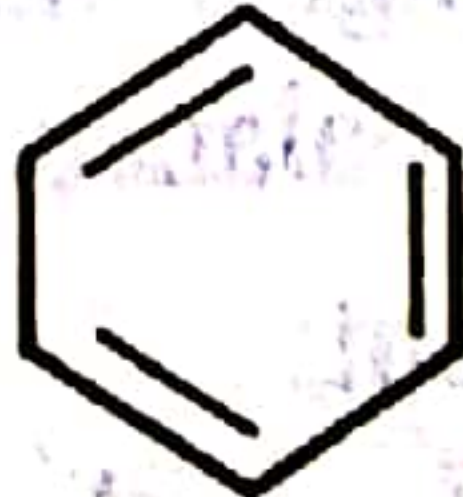Where 'Δm_w' and 'χ_w' are the parameters for water as reference standard. 'χ_a' is for the air having the value 0.03×10^{-6}. So, if we know 'Δm' for the substance under examination, the 'χ' can be calculated.

2.8.10 Magnetic susceptibility and molecular structure:

Molar magnetic susceptibility 'χ_m' is both an additive and constitutive property. The values of the atoms and groups of atoms can be calculated from the experimentally measured 'χ_m' values.

These values may be for double bonds, triple bonds and rings as shown in the following table (11).

Table (11). Atomic and structural susceptibilities of some important atomic and structural units:

| Atoms	Magnetic susceptibilities $\times 10^{-6}$	Structural factors	Magnetic susceptibilities $\times 10^{-6}$
H	−2.94	C = C	+5.35
C	−6.00	N = N	+1.91
O (R-OH and R-OR)	−4.62	C = N	+8.21
O (RCOR)	+1.74	C ≡ C	+0.80
O (RCOOR, RCOOH)	−3.38	C ≡ N	−0.81
N (open chains)	−5.58		
N (rings)	−4.61		−1.51
N (amines)	−1.55		
F	−11.6		
Cl	−20.2		
Br	−30.8		

The structure of a compound is proposed. Its theoretical magnetic susceptibility is calculated from the above table and compared with the experimental values. If the values are close to each other, then the structure is correct.

Examples:

(1) Methyl acetate has the following structure and experimental χ_m value is -43.6×10^{-6}. Theoretical χ_m value is also the same. So, the proposed structure is correct.

$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - O - CH_3$$
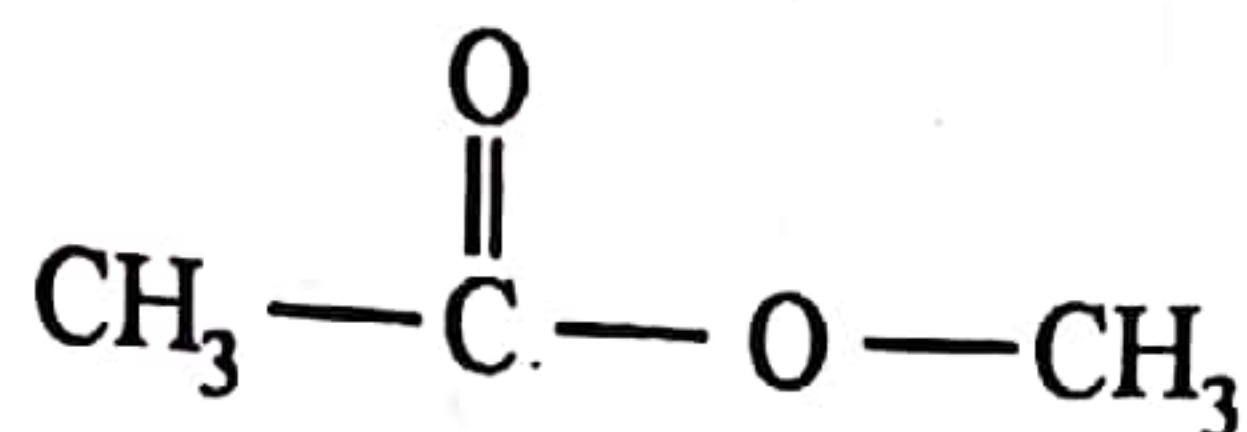
(2) The benzoic acid has the structure.
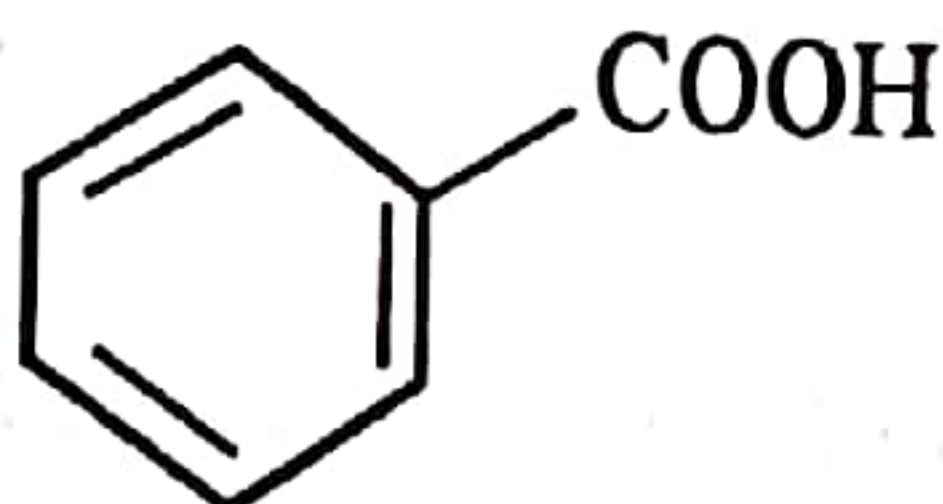
Its experimental and theoretical 'χ_m' is -70.3×10^{-6}. So, the proposed structure is correct.

2.8.11 Measurement of magnetic moment:

The magnetic property of a substance is due to the behaviour of each atom, ion or molecule because these microscopic particles behave like a micromagnet, with definite inherent magnetic moment of value μ_m. When such a substance is placed in the external magnetic field, then the micromagnet tend to arrange themselves parallel to the applied field.

Since, the molecule of a substance have the thermal motions, so the proper alignment is not possible. The actual arrangement taken up will depend upon the temperature. In 1905, Langevin gave the following relationship between molar magnetic susceptibility, magnetic moment and temperature.

$$\chi_m = Z \times \frac{\mu_m^2 N_A}{3kT} \qquad \dots \dots (9)$$

N_A = Avogadro's number

k = Boltzmann constant $= \left(\dfrac{R}{N_A}\right)$

Z = Proportionality constant which depends upon nature of substance.

μ_m = Magnetic moment

χ_m = Molar magnetic susceptibility.

Equation (9) is the equation of a straight line. If a graph is plotted between $\dfrac{1}{T}$ on x-axis and χ_m on y-axis then a straight line is obtained with positive

slope as shown in the following diagram. The slope of the straight line is

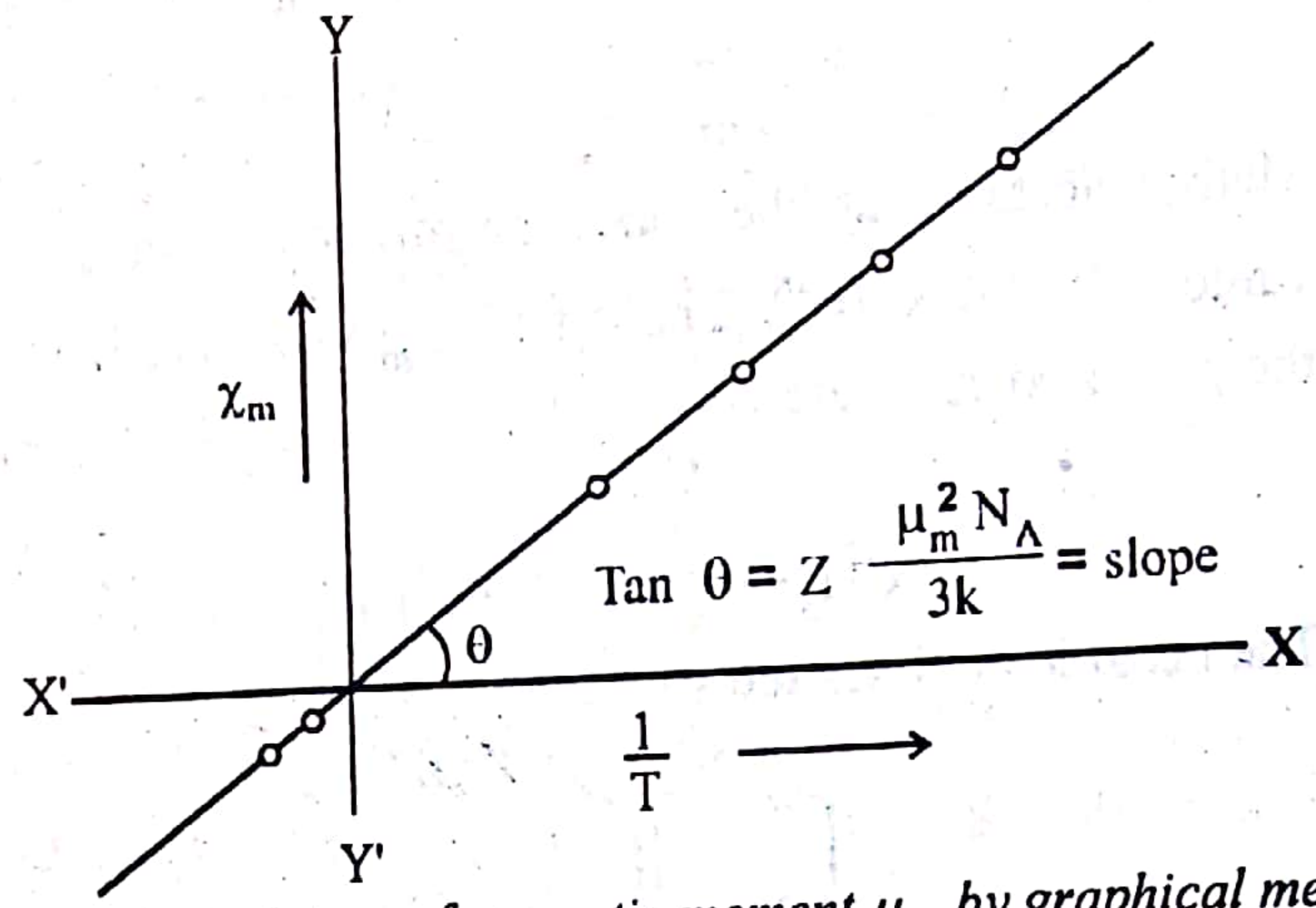$$Z \times \frac{\mu_m^2 \, N_A}{3k}$$ Fig (24). Hence, 'μ_m' can be calculated.

Fig. (24). Calculation of magnetic moment μ_m by graphical method.

2.8.12 Relationship of magnetic moment and number of unpaired electron:

The total magnetic moment of an atom, ion or a molecule is the sum of magnetic moment due to spin motions.

$$\text{Magnetic moment due to orbital motion} = \sqrt{\ell(\ell+1)} \text{ B.M.} \qquad \cdots\cdots \text{ (10)}$$

$$\text{Magnetic moment due to spin motion} = \sqrt{s(s+1)} \text{ B.M.} \qquad \cdots\cdots \text{ (11)}$$

'ℓ' is the azimuthal or orbital quantum number and 's' is the spin quantum number having value $\frac{1}{2}$. Now, let us consider an ion or a molecule instead of free atom. *In such situations the orbital motion of electrons are tied into nuclear configuration of the molecules. The electrons due to this reason are unaffected by the applied magnetic field.* So, the magnetic moment contribution due to orbital motion is negligible. It means that the magnetic moment of the molecule or the ion is mainly due to spin motion of the electron.

Hence, $\quad \mu_m = 2\sqrt{s(s+1)}$ B.M.

$\quad$'s' = Quantum number for one unpaired electron.

A molecule or ion has many unpaired electrons. So, the expression can be written as,

$$\mu_m = 2\sqrt{s(s+1)} \qquad\qquad\qquad \cdots\cdots \text{ (12)}$$

's' represents the total spin quantum number. For one unpaired electron $s = \frac{1}{2}$, for two electrons, $s = \frac{2}{2}$, for three electrons $s = \frac{3}{2}$ and for 'n' electrons $s = \frac{n}{2}$.

$$\mu_m = 2\sqrt{\frac{n}{2}\left(\frac{n}{2}+1\right)} \qquad\qquad \cdots\cdots \text{ (13)}$$

$$\mu_m = \sqrt{n(n+2)} \text{ B.M.} \qquad\qquad\qquad \cdots\cdots \text{ (14)}$$

Thus if we know the number of unpaired electrons, the value of μ_m can be calculated.

2.8.13 Applications of magnetic susceptibility measurement:

Important applications of magnetic susceptibility measurement are as follows.

1.   **Conformation of structure of molecules:**

We have mentioned in detail that 'χ_m' is additive and constitutive property both. If we compare the experimental and theoretical 'χ_m' values then we can verify the structure of the substances.

2.   **Calculation of number of unpaired electrons:**

We can determine χ_m in the laboratory and so the number of unpaired electrons can be calculated by doing the following substitution.

$$\text{Since, } \chi_m = Z \times \frac{\mu^2_m N_A}{3kT}$$

By taking 'μ_m', constant and putting the value of μ^2_m, we get

$$\chi_m = \frac{Z. N_A}{3kT} n(n + 2) \qquad \cdots\cdots (15)$$

Equation (15) can give us the value of 'n' which is number of unpaired electrons. The χ_m value of oxygen is found to be $- 4.62 \times 10^{-6}$, which can give us the value of 'n' as two. If means that oxygen is paramagnetic and it has two unpaired electrons.

3.   **Magnetic property of co-ordination complexes:**

Measurement of 'χ_m' can give us information about number of unpaired electrons in complexes.

$[Fe(F)_6]^{-3}$ has five unpaired electron because $F^{\ominus}$ is weak field ligand, while $[Fe(CN)_6]^{-3}$ has only one unpaired electron because $CN^{\ominus}$ is a strong field ligand.

4.   **Odd electron molecule:**

There are certain compounds which have odd number of electrons and so they are expected to be paramagnetic in nature. These gaseous substances are NO, NO_2 and ClO_2. Their magnetic susceptibility values tell us that they have one unpaired electron each.

5.   **Verification of formulas of certain compounds:**

H_2PO_3 is called hypophosphoric acid. It always exists in the form of dimer i.e., $H_4P_2O_6$. Their salts show the formulas as $Na_2H_2P_2O_6$ and $Ag_4P_2O_6$. Their salts do not have the formulas as $NaHPO_3$ and Ag_2PO_3. *The sodium and silver salts of this acid are diamagnetic but not paramagnetic.* Actually $NaHPO_3$ and Ag_2PO_3 should have odd number of electrons and should have been paramagnetic. Similarly, it is established that the chloride of Hg is Hg_2Cl_2 and not HgCl.