Physical Properties of Liquids

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Introduction

The Physical properties of a substance are those which could be studied & determined without causing any chemical change in it.

❖Properties of liquids:

1. The van der Walls forces of attraction in liquids is higher than the gases.

2. Thus the molecule in liquid state are held close together than in gases.

3. Hence density of liquid substance is much higher than gases.

4. A liquid may be regarded as a molten solid or a condensed gas.

5. There are appreciable force of attraction cohesive forces between the liquid molecules.

6. Most of the characteristic properties of liquid state are due to nature and magnitude of intermolecular forces of attraction.

TYPES OF PROPERTIES

PHYSICAL PROPERTIES

CHEMICAL PROPERTIES

❖ Classification of Physical Properties :

➢ There are number of physical properties which are used in determination of structure of molecules. They are divided into 4 classes as follows,

1. Additives Properties: These are properties which are the sum of the corresponding properties of their constituents. e.g. Mass, Molecular Weight, Molecular heat, dipole moment, Radioactivity etc.

2. Constitutive Properties: These are the properties which mainly depend on the constitution of molecule i.e. on the arrangement of atoms in molecule and smaller extent on their number and nature. e.g. Optical activity, structure of benzene due to contribution of six membered ring and three double bonds.

3. Additive and Constitutive Properties: These are the additives properties but the additive character is modified according to0 the arrangement of atom i.e. these properties are partly additive and partly constitutive. e.g. Parachor, Viscosity, Surface tension, molecular refractivity, atomic volume etc.

4. Colligative Properties: These are the properties which depend on the number of particles in the solution and not on their nature. e.g. Vapour pressure, osmotic pressure, elevation of boiling point, Depression of Freezing point etc.
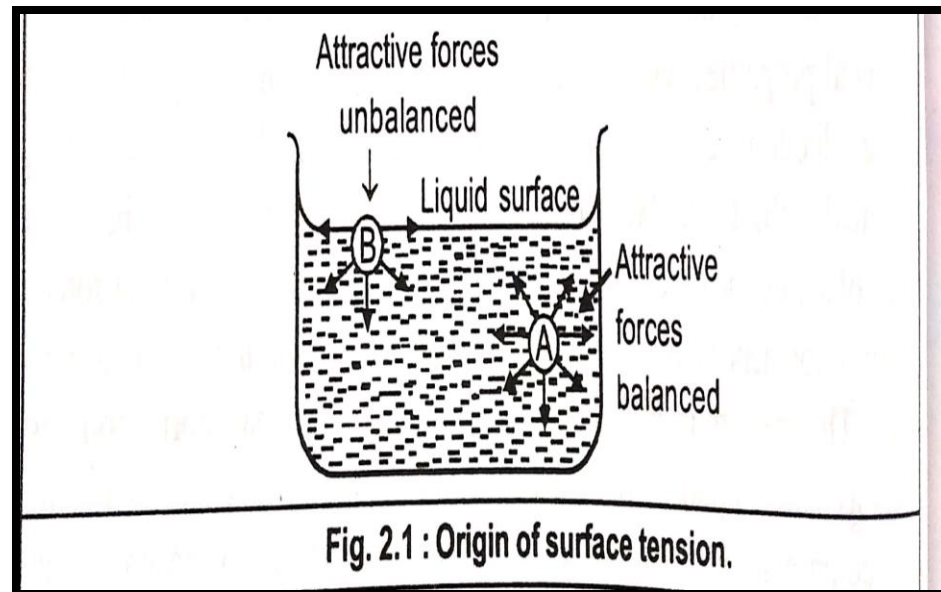
Surface tension

❖ **Surface Tension:** The existence of intermolecular forces of attraction in liquid is responsible for the phenomenon of surface tension.

➢ **Definition**: **The force in dynes acting at right angles to the line in the surface of liquid, one centimetre in length.**

Or

➢ **the force is assumed to act at right angles to the line in the liquid surface and its value for unit length of this line is called surface tension.**

Or

➢ **the energy required (work) required to expand the surface of a liquid by unit area .**

Fig. 2.1 : Origin of surface tension.

It is represented by Greek letter gamma (γ)
Expressed in **C.G.S. erg cm^{-2}, dynes cm^{-1}**
S.I. Nm^{-1} or Jm^{-2}
Due to surface tension, molecule tend to leave the surface. i.e. liquids tend to minimise their surface area.

Liquid	Surface Tension, γ	
	Dyne cm^{-1}	Nm^{-1}
Water	72.25	0.07275
Benzene	28.90	0.02890
Methanol	22.60	0.02260
Toluene	28.40	0.02840
Chloroform	27.10	0.02710
Ether	17.10	0.01710
Mercury	472.00	0.4720

Principle: The drops of the liquid under study are allowed to fall from the capillary glass tube. By counting the no. of drops for given volume of liquid and knowing weight of liquid drops, surface tension of liquid can be determined.
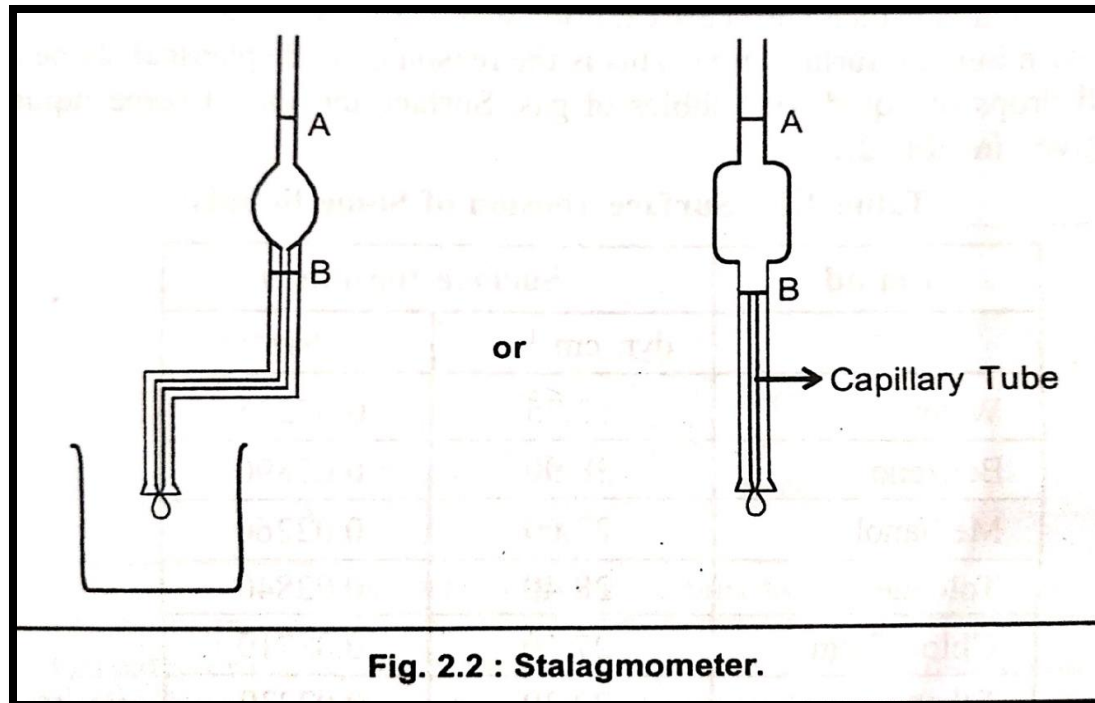
Construction and Working :

Fig. 2.2 : Stalagmometer.

Theory and Calculations

The drop is formed slowly at the capillary end. The hanging drop will detach when its weight (volume) reaches the magnitude balancing the surface tension of the liquid. The surface tension acting at outer circumference of the tube supports the drop in upward direction while the weight of drop pulls it in downward direction.

➤ The drop will detach when these two forces are balanced. Thus at the point of detachment, according to Tate's law,

$$W = 2\, \pi r \gamma \quad \text{…………(1)}$$

$$\text{i.e.} \quad mg = 2\, \pi r \gamma \quad \text{………..(2)}$$

Where, W= Weight, m= mass of the drop, g = acceleration due to gravity, r = outer radius of the tube, γ = surface tension of liquid.

➤ The drop falls when weight (W) is equal to circumference (2 $\pi r \gamma$) multiplied by surface tension of liquid (γ).

➤ Then by using reference liquid (usually water) surface tension of desired liquid can be determined by any one of the following methods.

Drop – Weight Method :

Certain number of drops of the given liquid are collected from stalagmometer and their weight is determined. Therefore weight of one drop can be calculated.

Similarly by using reference liquid weight of one drop is obtained.

From equation (2)

m1g = 2 πrγ1   ………..(3) – for liquid under study.

m1g = 2 πrγ1   ………..(4) – for reference liquid

Dividing equation (3) by (4)

$$\frac{\gamma 1}{\gamma 2} = \frac{m1}{m2} \qquad ………………..(5)$$

If water is used as reference liquid, then surface tension of desired liquid can be calculated as follows,

$$\gamma 1 = \frac{m1 \times \gamma 1\,H2O}{mH2O} \qquad ……………..(6)$$

Drop – number method :

In this method, number of drops are counted for a certain volume V from mark A to B in stalagmometer, for liquid and liquid 2. If n1 and n2 are no. of drops of liquid 1 and liquid 2 resply, then volumes of one drop are

V/n1 and V/n2 resply and masses of one drop are (V/n1)d1 and (v/n2)d2 resply where d is density.

Therefore from equation (5),

$$\frac{\gamma 1}{\gamma 2} = \frac{m1}{m2} = \frac{\left(\frac{V}{n1}\right)d1}{\left(\frac{V}{n2}\right)d2} = \frac{n2d1}{n1d1} \qquad \ldots\ldots\ldots\ldots(7)$$

By knowing d1 alongwith reference values γ2 and d2, surface tension of liquid under study i.e. γ1 can be calculated.

Differential Capillary rise method :

➢ Due to property of surface tension, the liquid moves up into a thin tube. i.e. capillary, which is called as capillary rise.

Principle : If the intermolecular attraction forces between liquid and capillary walls(adhesive), are stronger than those between the liquid molecules(cohesive), the liquid wet the walls and it rises in capillary upto certain level to form concave meniscus. This phenomenon is consequence of surface tension and it is applied to determine surface tension of liquids.

Fig. 2.3 : Schematic representation of capillary rise method.
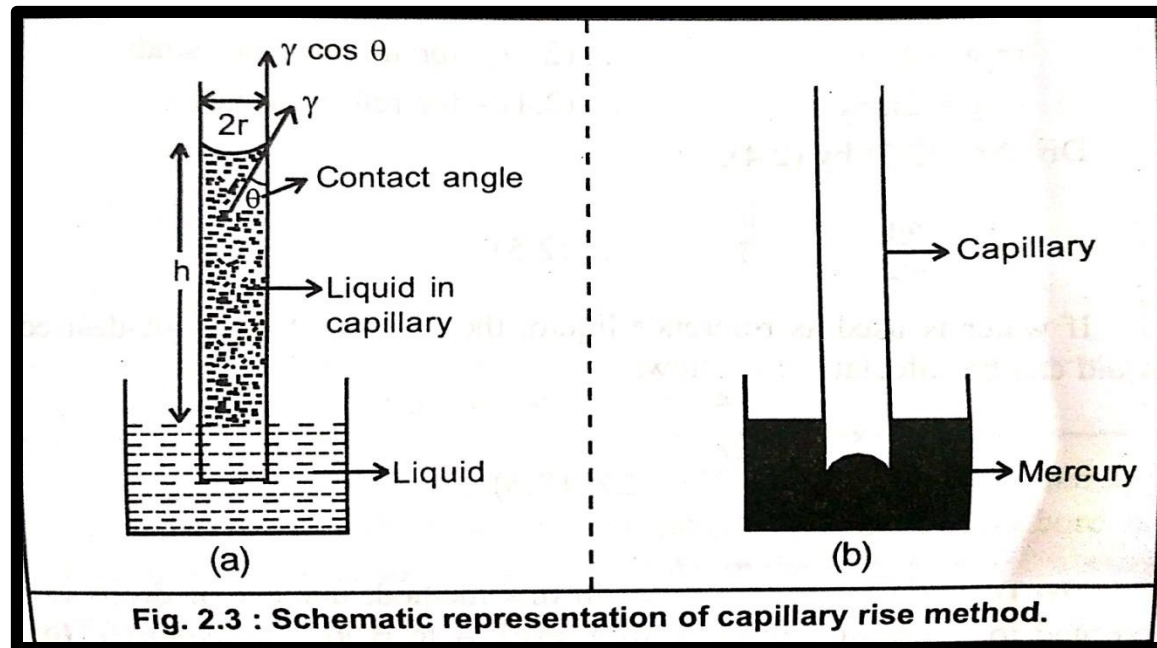
A capillary tube of radius r is dipped vertically into the liquid. The liquid enters into the liquid column of height 'h' having concave miniscus.

We know that, surface tension is the force per unit distance acting at a tangent to meniscus of surface.

Calculations :

If is the contact angle between tangent and capillary wall, γcosθ will be vertical(upward) component of surface tension. Then the total surface tension, raising the liquid column upward will be 2πr times the vertical component,

upward force = 2πr. γcosθ ....(1)

Where, r= radius of capillary, γ = surface tension, θ = contact angle.

For most of the liquids, wetting is perfect and θ is zero and cos θ = 1, then equation (1) reduces to,

upward force = 2πr. γ ....(2)

Now the force acting downward is due to weight of liquid column which is mass multiplied by gravitational pull.

downward force = m × g

= V × d × g ....(3)

Where, V = Volume of liquid column, d = density of liquid

We have, $V = \pi r^2 \cdot h$

Downward force $= \pi r^2 \cdot h\, d\, g$ ....(4)

At equillibrium, upward force = downward force

$2\pi r \cdot \gamma = \pi r^2 \cdot h\, d\, g$ ....(5)

$$\gamma = \frac{\pi r \cdot h\, d\, g}{2} \qquad ....(6)$$

By knowing r, h, d surface tension of the liquid can be calculated. If the liquid is not perfectly wetting the capillary, i.e. $\theta \neq 0$, then equation (6) becomes

$$\gamma = \frac{r \cdot h\, d\, g}{2\cos\theta} \qquad ....(7)$$

On the contrary, when capillary is dipped in liquid mercury, the upper level of liquid in the tube at low level than the surface of free liquid with convex meniscus. Here cohesive is greater than adhesion resulting in depression in liquid level in capillary.

VISCOSITY

Viscosity is one of the physical property and exhibited by both liquids as well as gases.

Viscosity is associated with flow of liquid.

Some liquids flow readily or ast these liquids are having low value of coefficient of viscosity and are known as mobile liquids. E.g. Ether, alcohol, acetone etc. but some liquids flow slowly & these liquids are having high value for coefficient of viscosity known as viscous liquids. E.g. Glycerin.

The property of liquids which determines their rate of flow is called Viscosity of liquid.

The rate of flow depends on the nature of liquid and the force which produces the flow.

Layers of Molecules of
the Liquids of
on glass plate

4 ⟶
3 ⟶
2 ⟶
1 ⟶
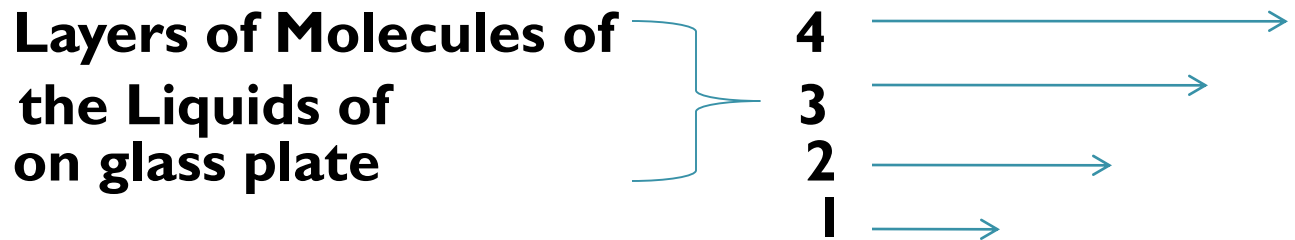
The liquid layer immediate contact with a glass plate i.e. fixed surface is stationary and the velocity of layers increases with the distance from the fixed surface.

Thus there is a movement of different layers past one another in the direction of flow.

Defⁿ :The internal friction of the liquid which makes the liquid to flow with different velocities is also known as the viscosity of the liquid.

The force of friction per unit area required to maintain the velocity difference (v/ Sec) is directly proportional to the velocity **v** difference of the two adjacent layers, And inversely proportional to the distance **x** between them.

$$\text{Force (F)} \quad \alpha \quad \frac{v}{x}$$

$$\text{Force (F)} \ = \ \eta \ \times \ \frac{v}{x}$$

Where η is proportionality constant and known as coefficient of viscocity.

Coefficient of Viscosity (η) : The coefficient of viscosity or in brief, the viscosity can be defined as, **" the force per unit area required to maintain unit difference of velocity between two parallel layers in the liquid, unit distance apart."**

Units of Viscosity : The coefficient of viscosity is expressed as follows,

C.G.S. : poise (P) **or** millipoise (m P) **or** micropoise (μ P) **or** dyne.cm^{-2}.sec.

Where 1dyne.cm^{-2}.sec. = 1Poise

S.I : Nm^{-2}.sec **or** Pascal(Pa) sec. **or** Kg m^{-1}s^{-1}.

FLUIDITY

The reciprocal of coefficient of viscosity is called as fluidity and is denoted by symbol, Ø (Greek Phi).

$$\text{i.e.} \quad \text{Fluidity, Ø} = \frac{1}{\eta}$$

Fluidity is a measure of the ease with which a liquid can flow. **The viscosities of most liquids decreases with increasing temperature.**

Viscosities of liquids in Pa sec (Kg m^{-1} s^{-1})

Liquid	Temperatures		
	0 K	298 K	323 K
Water	0.001793	0.000895	0.000549
Ethanol	0.001790	0.00109	0.000698
Benzene	0.00090	0.00061	0.00044

Determination of Viscosity by Ostwald Viscometer

The coefficient of viscosity η of a liquid
can be determined by using following formuladerived by Poiseuille.

$$\eta = \frac{P \; \pi \; r4 \; t}{8 \; v \; l}$$

where, t = time required for v ml of liquid to flow through a capillary tube
of length ' l ' and radius 'r' under an applied pressure 'P'.

❖ **Experimental procedure :**

1. A definite volume of the liquid under examination is put into the wide arm of viscometer.
2. And sucked up through the narrow arm, slightly above the mark A.
3. The liquid is now allowed to flow back and the time of flow of liquid from mark A to B is noted.
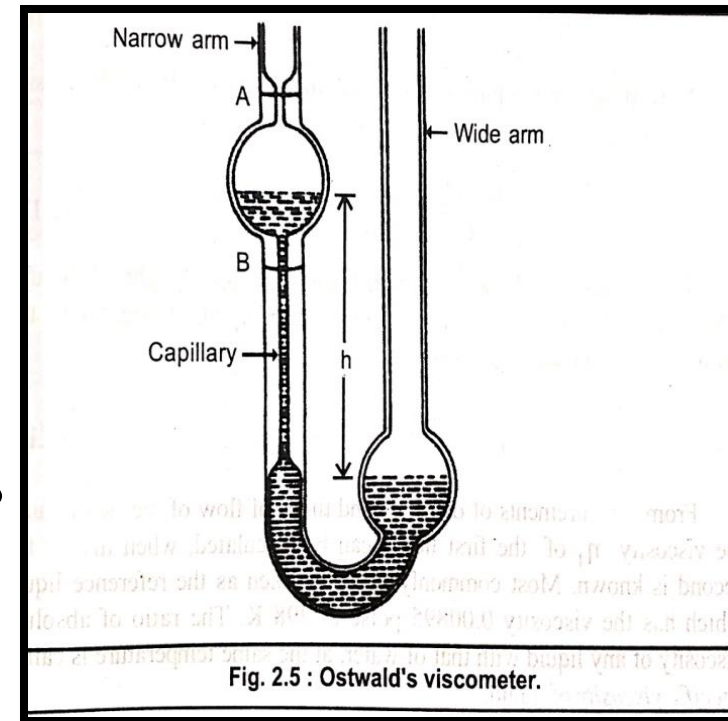5. The whole process is then reapeted for second liquid whose viscosities known.

Fig. 2.5 : Ostwald's viscometer.

Calculations

It is found that the pressure P, that causes the flow of liquid, depends on the difference in height "h" of liquid level in the two arms, the density of liquid "d_1" and acceleration due to gravity "g" hence equation becomes,

$$\eta_1 = \frac{P \pi r4 \ t}{8 \ v \ l} \qquad d_1.t_1$$

Now if the same volume of second liquid of viscosity η_2 and density d_2, takes t_2 seconds to flow through the same capillary, then,

$$\eta_2 = \frac{P \ \pi r4 \ t}{8 v \ l} \qquad d_2.t_2$$

The values of volume v, length l, radius r, and height h, through which liquid falls are the same in case of each liquid.

Hence, taking the ratio of above equations get, $\dfrac{\eta 1}{\eta 2} = \dfrac{d1 \ . \ t1}{d2 \ . \ t2}$

From the measurement of densities and time of flow of the two liquids, the viscosity η_1 of first liquid can be calculated, when that of second is known.

Specific viscosity : The ratio of absolute viscosity of any liquid with that of water, at the same temperature is called specific viscosity.

Advantages :

1. Very convenient apparatus for determination of viscosity.
2. Viscosity at different temperatures can be determined.

Refractive Index (Snell's law)

➢ When light passes from one medium to another, it suffers refraction i.e. a change of direction

➢ When angle of refraction "r" is less than the angle of incident, i. this is called refraction of light.

Diagram

Fig. 2.6 : Refraction of light.
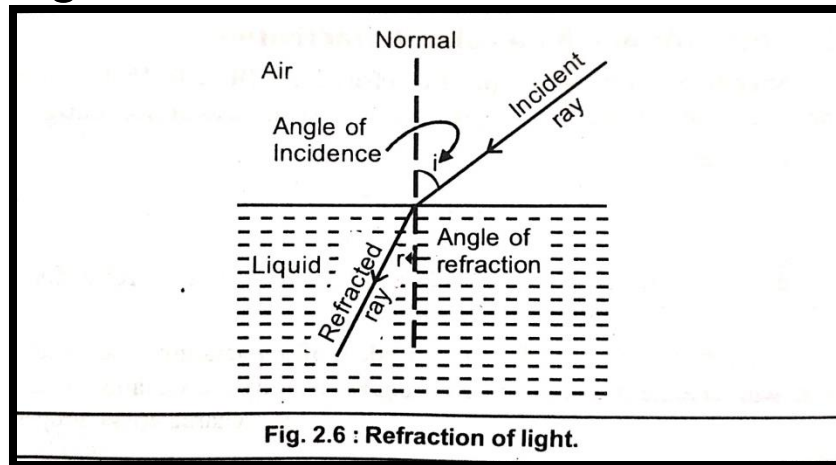
The ratio of the since of the angle of incidence and that of refraction is constant and characteristic of the liquid or solid considered. This is known as **Snell's law.**

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

where n = refractive index of the liquid or solid

i.e. n is refractive index of the second medium with respect to the first.

The **refractive index** of a medium also defined as, **the ratio of the velocity of the light in vacuum to that in the medium.**
i.e

$$n = \frac{\text{Velocity of light in vacuum}}{\text{Velocity of light in the medium}}$$

when, the angle of incident i = 90^0 then,
    sin i = sin 90^0 = 1

Hence above equation becomes,
$$n = \frac{1}{\sin r}$$

Refractive index measured by optical instruments called **Abbe Refractometer.**
Refractive index has no diementions.
The value of refractive index **increases with decrease in temperature and decrease in wavelength of the light.**

Specific Refraction and Molecular refractivity

Specific Refraction or Specific Refractivity (R) :

Lorentz and Lorenz derive the relationship, on the basis of electromagnetic theory of light.

$$R = \frac{n2 - 1}{n2 + 2} \times \frac{1}{d}$$

Where, n = refractive index

d = density   R = Specific refraction

constant quantity R is independent of temp.

The variation in 'n' with change of the temp. is compensated by variation in 'd'.

R depends only on nature of the substance.

Molecular (Molar) Refraction or Molecular refractivity (R_M)

The product of molecular weight (M) and Refractivity (R) is called molecular or molar refractivity (R_M) and is given by,

$$R_M = R \times M$$

$$R_M = \frac{n2 - 1}{n2 + 2} \quad \frac{M}{d}$$

The value of R_M is characteristic property of the substance and remains constant with temperature.

Unit : cm^3 per mol.

Measurement of Refractive Index by Abbe's Refractometer

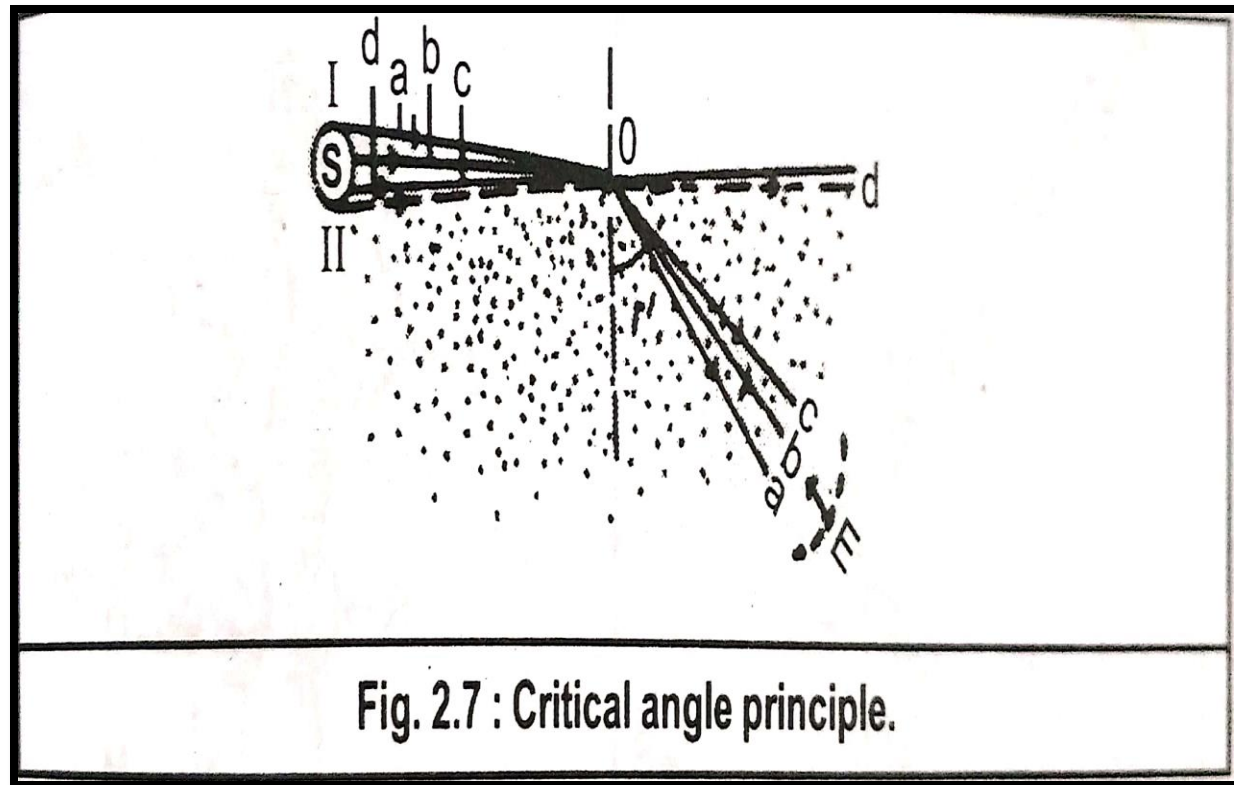Principle : The refractive index of various liquids is measured on the basis of *Critical angle principle.*

Fig. 2.7 : Critical angle principle.

Abbe's Refractometer

Principle : The refractive index of various liquids is measured on the basis of *Critical angle principle.*

Construction and Working
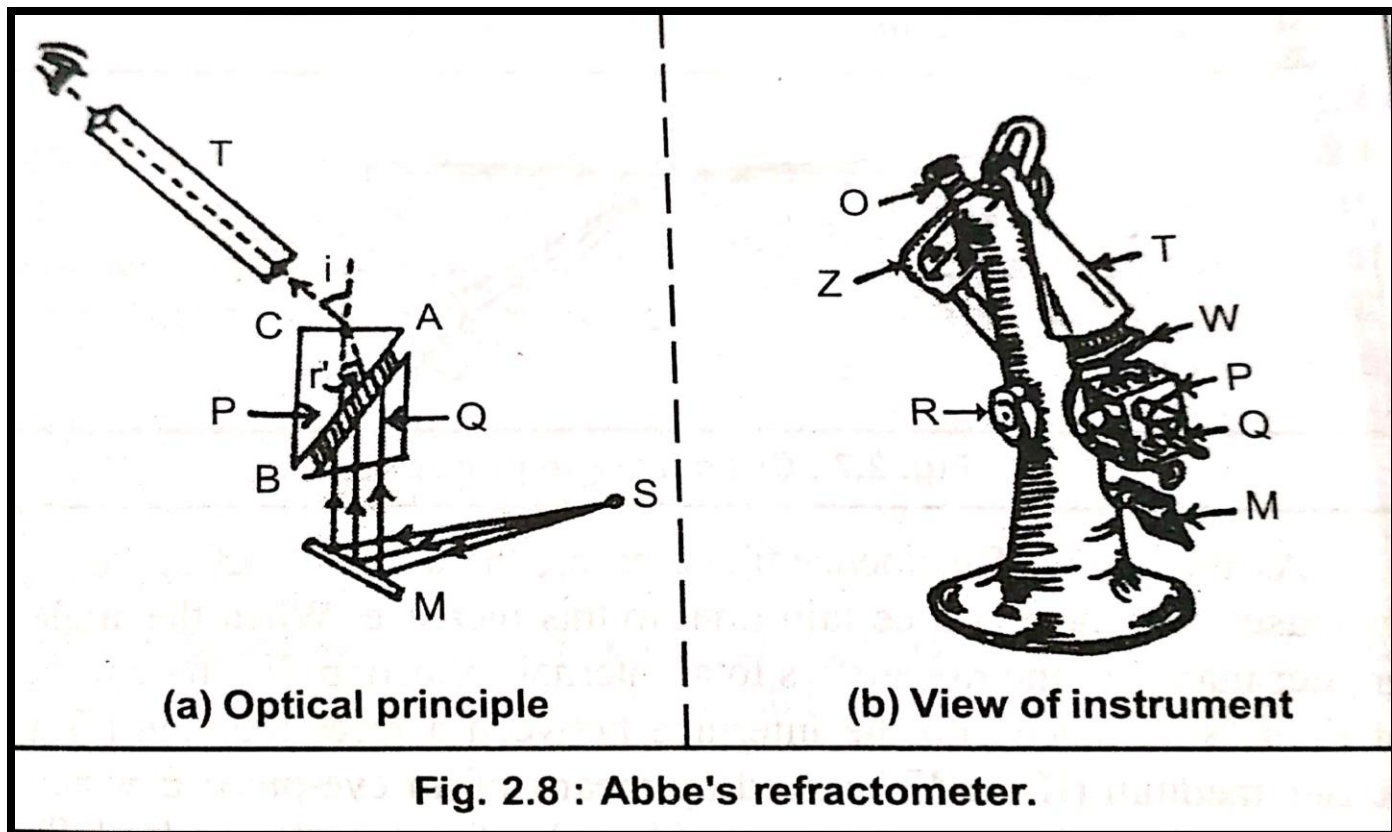

(a) Optical principle

(b) View of instrument

Fig. 2.8 : Abbe's refractometer.

Advantages :

1. Easy to handle.

2. Only few drops of liquid are required.

3. Refractive index of liquid can be measured directly and quickly.

4. Temperature can be controlled.

5. Refractive index range is from 1.3 to 1.7 with an accuracy of ± 0.0002 units.

Molecular Refractivity And Chemical Constitution

➤ Molecular refractivity is a sort of molecular volume hence it is Additive and Partly Constitutive Proprty. E.g. In a homogeneous series of aliphatic compounds, a difference of –CH2 group in composition makes difference of 4.618 in the molar refractivity.

➤ Since it is depends upon the number, nature and arrangement of atoms or strucural units in the molecule.

➤ It may be used to study the strucure of molecules.

➤ and for this purpose, calculated values of molar refractivities are compared with observed or experimental values.

Atomic And Structural Refractivities

Element	Refractivity	Structural Unit	Refractivity
Hydrogen	1.1	O (In OH group)	1.53
Carbon	2.42	O (In >c=o Group)	2.21
Chlorine	5.97	O (In Ethers)	1.64
Bromine	8.86	Ethyl radical	10.3
Iodine	13.90	Methyl radical	5.65
Structural Unit	**Refractivity**	C= O group	4.601
3, Carbon ring	0.71	-OH group	2.55
4, Carbon ring	0.48	-CN group	5.46
5, Carbon ring	− 0.19	-COOH group	7.23
6, Carbon ring	− 0.15	-NO_2 group	6.71
N (Pri. Amines)	2.32	-CH_2 group	4.618
N (Sec. Amines)	2.50	Double bond	1.730
N (Tert. Amines)	2.84	Triple bond	2.40

Determination of Refractivity by the use of refractivity values :

1. Kekule's formula for benzene is, as given below.
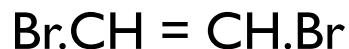
Calculation of molar Refractivity
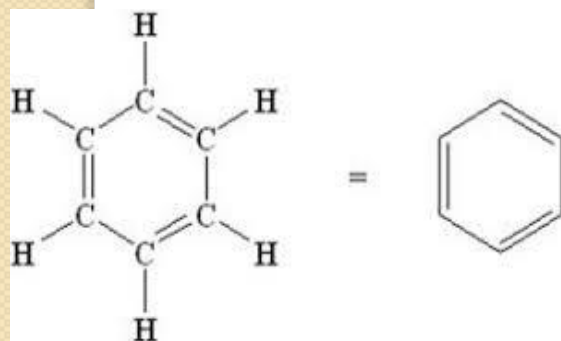
6 C	6 × 2.42 = 14.52
6 H	6 × 1.10 = 6.60
3 double bonds	3 × 1.73 = 5.19
1 Six Membered ring	1 × (−0.15) = −0.15
Total (R$_M$)	**26.16**

The experimental value of (R$_M$) is 26.15, which suggests that Kekule's formula of Benzene is correct.

2. Formula of Acetylene dibromide is as given below
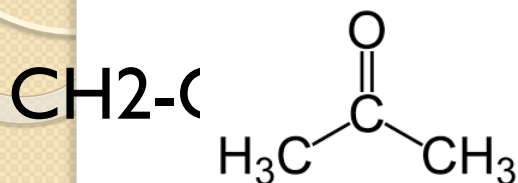
Br.CH = CH.Br

Calculation of molar Refractivity

2 C	2 × 2.42 = 4.84
2 H	2 × 1.10 = 2.20
2 Br	2 × 8.86 = 17.72
double bonds	1 × 1.73 = 1.73
Total (R_M)	**26.49**

The observed value of (R_M) is 26.30.

The two values are fairly close to each other and confirm that above structural formula for acetylene dibromide.
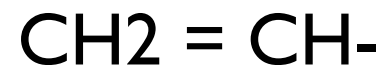
3. A molecule having the formula C_3H_6O may be either,

Acetone   Allyl Alcohol

OR   CH2 = CH-

CH2-C

Its molecular refraction for sodium D- Line is 16.974.

Calculation of molar Refractivity

For Acetone		For Allyl Alcohol	
3 C	3 × 2.42 = 7.26	3 C	3 × 2.42 = 7.26
6 H	6 × 1.10 = 6.60	6 H	6 × 1.10 = 6.60
1 C=O group	1 × 2.21 = 2.21	1 double bond	1 × 1.73 = 1.73
Total	**16.07**	1 O in OH	1 × 1.53 = 1.53
		Total	17.12

Since, calculated (R_M) value of Allyl alcohol (17.12) is quite close to experimental value (16.974), the compound must be allyl alcohol rather than acetone

THANK YOU