1.2.6 Kinetic energy of one molecule of an ideal gas:

If we divide the equation (4) with Avogadro's number N_A, then we get the equation for one molecule of gas i.e. e_k:

$$E_k = \frac{3}{2}RT$$

$$e_k = \frac{E_k}{N_A} = \frac{\frac{3}{2}RT}{N_A} \qquad \frac{R}{N_A} = k \ (\text{Boltzmann's constant})$$

$$e_k = \frac{3}{2}kT \qquad\qquad\qquad\qquad \text{...... (5)}$$

The value of $k = R/N_A$ is, $1.38 \times 10^{-23}\ JK^{-1}$ molecule^{-1}.

This equation (5) gives us the translational energy of a monoatomic gas.

1.3.0 COLLISION DIAMETER, COLLISION FREQUENCY, COLLISION NUMBER AND MEAN FREE PATH:

Introduction:

In the kinetic molecular theory of gases, we come to know that the molecules of a gas are moving randomly, colliding among themselves and with the walls of the vessel. During the collisions, they suffer a change in their directions and also change their velocities. The time for which the two molecules are in contact at the time of collision is called compression time.

Since, we are going to discuss the frequency of the collisions and the free path in between the collisions, so first of all we should know about the nature of the collisions.

The collisions are of three types.

(i) Grazing collision or glancing collision:

"In these collisions, the molecules are moving just parallel to each other, with the average velocity $(\bar{c})$ and their outer boundaries touch each other." The following diagram shows the grazing collisions. Fig. (2) (a)
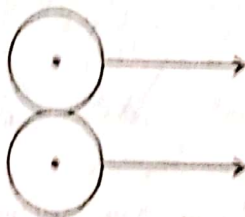

Fig. (2) (a) Grazing collision (relative velocity $\bar{c}$).

(ii) Head on collision:

"When two molecules approach each other on a straight line, then they collide head to head and the collision is head on." The approaching molecules retrace the straight line path in the reverse direction. The relative speed becomes $2\bar{c}$. Following diagram 2(b) shows the head on collision.
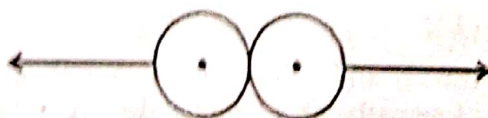

Fig. (2) (b) Head on collision (relative velocity $2\bar{c}$).

(iii)   **Right angled collision:**

When two molecules approach each other and their approaching lines are approximate $90°$ *to each other. Then the collision is right angled.* The relative speed is ' $\sqrt{2}\bar{c}$ '. Follow diagram 2(c) shows this collision
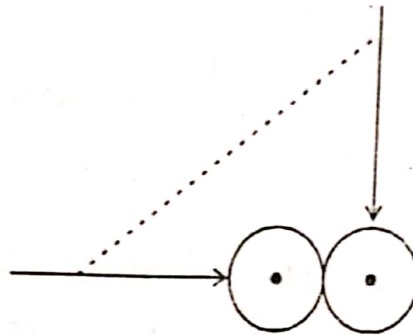

Fig. (2) (c) Right-angled collision (relative velocity $\sqrt{2}\bar{c}$)

Elastic collision:

During the collisions there happens a change in the direction of the motion but tota energy remains the same. *The collisions in which there is no net loss or gain of energy are calle elastic collisions.*

1.3.1   Collision diameter:

In order to do the collision, the molecules approach each other. At the time of contact c the outer boundaries, there is a limit beyond which they cannot come close to each other. This is called the distance of closest approach. *"The closest distance between the centers of two molecules taking place during collision is called collision diameter."* Collision diameter is represented by σ. Fig. (3).

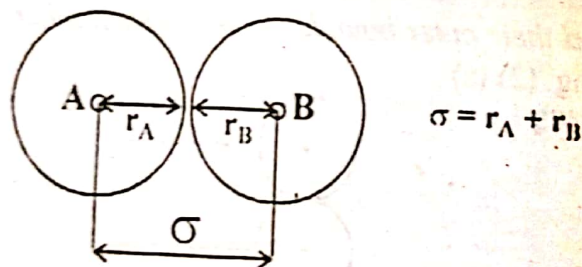The following diagram shows that the collision diameter is equal to the sum of radii of the two particles.

$$\sigma = r_A + r_B$$

Fig. (3) Collision diameter of two colliding molecules

1.3.2   Collision frequency (Z_1):

"If we follow a single molecule in one cm³ of the gas, and want to observe that, how many collisions are being faced by this molecule in one second, then it will be collision frequency of that molecule." It is denoted by Z_1. Its value should depend upon the velocity of gas molecules, sizes of molecules and closeness of the molecules in the vessel.

1.3.3   Mean free path (λ):

When a molecule travels and collides with various molecules, then it travels free path in the vessel. Anyhow, all the free paths of the molecules are not equal. So, if we take the average of

all these free paths, then we get the mean free path. *"Hence, mean free path is average distance covered by a molecule between two successive collisions."* It is denoted by 'λ'.

Mathematically, 'λ' is related to the mean distance travelled by the molecule in one second and its number of collisions per second.

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$$\lambda \doteq \frac{\text{mean velocity of molecule}}{\text{collision frequency}}$$

$$\lambda = \frac{\bar{c}}{Z_I} \qquad \cdots\cdots (1)$$

1.3.4 Collision number (Z_{II}):

"It is the number of collisions happening in all the molecules in 1 cm³ of the gas in one second." It is denoted by 'Z_{II}'. Mathematically, we can say that,

$$Z_{II} = \frac{nZ_I}{2} \qquad \cdots\cdots (2)$$

'nZ_I', is divided by 2, so that each collision may not be counted twice.

1.3.5 Derivation for the expression of collision frequency (Z_I):

Consider a molecule 'A' which is travelling in the center of imaginary cylinder from left to the right. This imaginary cylinder is supposed to be present in the vessel of a gas. Diameter of this cylinder is '2σ'. The diameter of the molecule itself is 'σ'. It means that two molecules can travel in this imaginary cylinder simultaneously. The average velocity of the molecule travelling in the centre of the cylinder is '$\bar{c}$' ms⁻¹. If the length of the imaginary cylinder is supposed to be '$\bar{c}$' meters, then it means that the molecule 'A' will approach the other end of the cylinder in one second. Following diagram (4) makes the idea clear.
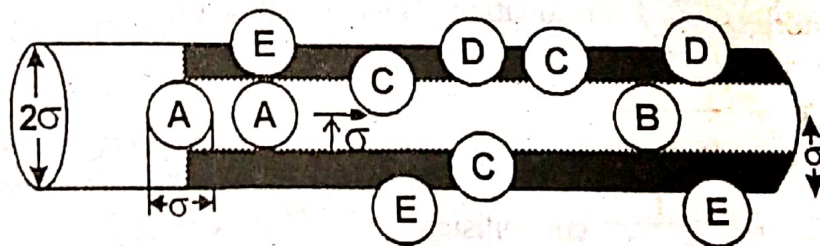

Fig. (4) Imaginary cylinder has many molecules and one molecule (A) is travelling in the centre of the cylinder.

There are many molecules present in this imaginary cylinder. The categories of molecules are 'B', 'C', 'D' and 'E'. The molecule 'A' can collide with 'B' type molecules doing head-on collisions, with 'C' type, right-angled collisions with 'D' grazing collisions and there will be no collision with molecules of the type 'E'. Keep it in mind, that there are many molecules of each category in this cylinder.

Now, the question arises, that how many collisions this molecule 'A' will face while moving from one end of the cylinder to the other end.

Its answer is that number of collisions depend upon the number of molecules in this imaginary cylinder.

How to count the number of molecules? It is very easy.

Let the radius of imaginary cylinder is $= \sigma.$

Base area of this imaginary cylinder $= \pi\sigma^2$

Length of the cylinder in meters $= \bar{c}$

Volume of the imaginary cylinder $= \pi\sigma^2\bar{c}$

Let the number of molecules in one cm^3 $= n$

Number of molecules in imaginary cylinder $= \pi\sigma^2\bar{c}\, n$

So, the number of collisions which the molecule 'A' will experience in one sec should be $= \pi\sigma^2\bar{c}\, n.$

Be careful, that the number of right-angled collision is much greater than graz collisions and head-on collisions. So, the exact number of such collisions should be $\sqrt{2}\pi\sigma^2\bar{c}\, n.$

We have multiplied with '$\sqrt{2}$', because the relative speed of two molecules approach each other to do right-angled collision, is '$\sqrt{2}\bar{c}$', and not '$\bar{c}$'. It means that considering the rig angled collisions, the length of the imaginary cylinder is proposed to be ' $\sqrt{2}\bar{c}$ '.

Hence, $Z_I = \sqrt{2}\pi\sigma^2\, \bar{c}n$ $\cdots\cdots$ (3)

This is the collision frequency of the molecule.

1.3.6 Formula of mean free path (λ):

As we have previously explained that mean free path is the ratio of $\bar{c}$ and Z

$$\lambda = \frac{\bar{c}}{Z_I}$$

      $\cdots\cdots$ (4)

Putting value of Z_I from equation (3) into equation (4)

$$\lambda = \frac{\bar{c}}{\sqrt{2}\pi\sigma^2\bar{c}\, n}$$

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2\, n} \text{ cm collision}^{-1}$$

      $\cdots\cdots$ (5)

According to the equation (5), the mean free path of the gas molecule is inversel proportional to the square of the collision diameter and inversely proportional to the number c molecules per unit volume. It means, greater the number of molecules per unit volume, small the distance the molecule has to the cover between successive collisions.'

1.3.7 Formula of collision number (Z_{II}):

"Collision number is the number of collisions happening in all the molecules in on second in 1 cm^3 of the gas."

We know that number of collisions of a single molecule, called the collision frequency is Z_I. If we multiply 'Z_I' with 'n' and divided with 2, then we get the total number of collisions in one second in one cm^3.

$$Z_{II} = \frac{nZ_I}{2}$$

We have divided it with two, because each collision involves two molecules and collision is not the property of a single molecule. The division with two, is to be done so that each collision may not be counted twice.

$$Z_{II} = \frac{n Z_I}{2} = \frac{n \sqrt{2} \pi \sigma^2 \bar{c} \, n}{2}$$

$$Z_{II} = \frac{\pi \sigma^2 \bar{c} \, n^2}{\sqrt{2}} \qquad \qquad \dots \dots (6)$$

According to the equation (6), the collision number depends upon the collision diameter, number of collisions cm^{-3} and the average velocity '$\bar{c}$'.

The expression for average velocity is

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

It means that, average velocity depends upon the temperature and the molar mass. Indirectly, we can say that the collision number Z_{II} is,

(i)   directly proportional to square root of temperature.

(ii)   inversely proportional to square root of molar mass.

(iii) directly proportional to square of collision diameter.

(iv)   directly proportional to square of number of molecules per unit volume.

EXAMPLE (4)

Oxygen is maintained at 1 atm. pressure and 25°C. Calculate: (i) Number of collisions s^{-1} molecule^{-1}, (ii) Number of collisions s^{-1} m^{-3}. The collision diameter of oxygen molecule is 3.60×10^{-10} m.

SOLUTION:

First of all we calculate average velocity, $\bar{c}$

Data:

Molar mass of O_2 $= 32 \times 10^{-3}$ kg mol^{-1}

Temperature $= 25\,C° + 273 = 298$ K

R $= 8.3143$ JK^{-1} mol^{-1}

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

By putting values

$$\bar{c} = \sqrt{\frac{8 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{3.14 \times 0.032 \text{ kg mol}^{-1}}}$$

$$\bar{c} = 4.44 \times 10^2 \text{ ms}^{-1}$$

Number of molecules = Number of moles × Avogadro's number

$$= n \times N_A = \frac{PV}{RT} \times N_A \quad \boxed{\text{Since } n = \frac{PV}{RT}}$$

$$V = 1 \text{ dm}^3$$

Putting values

$$\text{Number molecules} = \frac{(1 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})}{(0.0821 \text{ atm K}^{-1} \text{ mol}^{-1}) \times 298 \text{ K}} = 0.246 \times 10^{23}$$

$$= 2.46 \times 10^{25} \text{ m}^{-3}$$

$$= 2.46 \times 10^{22} \text{ dm}^{-3}$$

$$= 2.46 \times 10^{25} \text{ m}^{-3}$$

The collision frequency is the number of collisions per second.

Since $1 \text{ dm}^3 = 10^{-3} \text{ m}^3$

(i) $Z_1 = \sqrt{2} \pi \sigma^2 \bar{c} n$

$Z_1 = 1.414 \times 3.14 \times (3.60 \times 10^{-10} \text{ m}^2)$
$\quad \times (4.44 \times 10^2 \text{ ms}^{-1}) \times (2.64 \times 10^{25} \text{ m}^{-3})$

$Z_1 = \boxed{6.74 \times 10^9 \text{ s}^{-1}}$ Ans

The collision number is the number of collision per second per m³

(ii) $Z_{11} = \dfrac{\pi \sigma^2 \bar{c} n^2}{\sqrt{2}}$

$$Z_{11} = \frac{3.14 \times (3.60 \times 10^{-10})^2 \times (4.44 \times 10^2) \times (2.46 \times 10^{25})^2}{1.414}$$

$Z_{11} = \boxed{7.73 \times 10^{34} \text{ collisions s}^{-1} \text{ m}^{-3}}$ Ans.

1.4.0 DEVIATION OF GASES FROM IDEAL BEHAVIOUR

These gases which obey the Boyle's law, Charles's law or general gas equation are said to be ideal. In order to check the ideality of a gas, we can plot a graph between "$n = \dfrac{PV}{RT} = Z$", and the pressure of the gas for one mole of gas. In the case of ideal gas, a straight line is expected parallel to the pressure axis showing that for one mole of a gas the compressibility factor (Z) should be one.

Anyhow, it has been observed that the most common gases like H_2, N_2, He, CO_2 etc. do not follow the straight line as shown in the diagram (5). It means that the product of P and V does not remain constant, at constant temperature
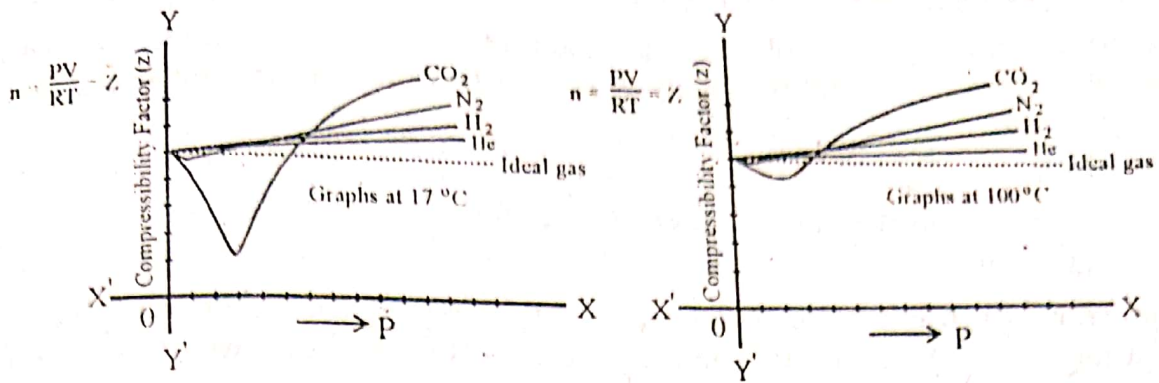
Fig. (5) Graphical explanation of effect of pressure and temperature on compressibility factor $Z = \dfrac{PV}{RT}$

The graphs of the gases at 17°C, show more deviations from ideal behaviour than at 100°C. Moreover, the extent of deviation of these gases are more prominent at high pressures. We draw the important conclusion from the above graphs.

   (i)   The gases are comparatively ideal at high temperature and low pressures.

   (ii)   The gases become non-ideal at low temperature and high pressures.

1.4.1 Causes for deviation from ideality:

Kinetic theory is the foundation stone of all the gas laws and the general gas equation. There are two faulty assumptions in the kinetic theory of gases.

    Let us recall these faulty assumptions and then try to find the remedy for them.

   (i)   Actual volume of gas molecules is negligible as compared to the volume of the vessel.

   (ii)   There are no forces of attractions among the molecules of gases.

Both these postulates are correct, at low pressures and high temperatures and these postulates become wrong at low temperatures and high pressures.

    Actually, low temperature and high pressure become responsible for creation of forces of attractions and moreover, actual volume does not remain negligible.

    It is necessary to account for the actual volume and mutual attractions of molecules. This job was done by Van der Waal.

1.4.2 Van der Waal's equation:

Van der Waal modified the general gas equation and performed the corrections i.e., volume correction and pressure correction.

Volume correction:

    Van der Waal thought that some of the volume of the vessel is occupied by the molecules of the gas and that volume is not available for the free movement of the molecules. Actually, we need the free volume of the gas and that is obtained when we subtract the volume of molecules from the volume of the vessel.

$$V_{free} = V_{vessel} - V_{molecule}$$

Let V_{free} is 'V' and $V_{molecule}$ is 'b' for one mole of a real gas.

So, $V = V_{vessel} - b$ ...... (1)

This 'b' is called effective volume of gas molecules. Keep it in mind that 'b' is not the actual volume of gas molecules, but is roughly equal to 4 times their molar volumes. If we have one mole of a gas, then

$$b = 4V_m$$

V_m = actual volume of gas molecules for one mole of the gas.

Pressure correction:

The pressure which is exerted on the walls of the vessel is due to collisions. Since there are forces of attraction, so the molecules can not hit the walls of the vessel with that much force, with which they should have been in the absence of attractive forces.

It means that the pressure being observed on the walls of the vessel is a little bit less than the ideal pressure.

$$P_{observed} = P_{ideal} - P_{lessened}$$

The pressure which is being lessened is denoted by P'.

Let us say that $P_{observed}$ = P and $P_{lessened}$ is denoted by P'.

$$P = P_i - P'$$

$$P_i = P + P'$$

The value of P' given by Van der Waal is $\frac{a}{V^2}$.

$$P' = \frac{a}{V^2}$$

In order to estimate the value of P' which is lessened pressure, we proceed as follows.

Suppose we have two types of molecules A and B. Let the concentrations of A and B type molecules are C_A and C_B. The force of attraction between A and B is proportional to C_A and C_B. So,

$$P' \propto C_A C_B$$

Now suppose that "n" is the number of moles of A and B separately. Hence $\frac{n}{V}$ is the number of moles dm^{-3} of A and B separately. "V" is the volume of the vessel containing the gas. So,

$$P' \propto \frac{n}{V} \cdot \frac{n}{V}$$

$$P' \propto \frac{n^2}{V^2}$$

$$P' = \frac{an^2}{V^2}$$

where   a = constant of proportionality

If the number of moles of gas is unity, then n = 1

$$P' = \frac{a}{V^2}$$

Pressure of the ideal gas $P_i = P + P'$

So, $P_i = P + \dfrac{a}{V^2}$ ...... (2)

'a' is the co-efficient of attraction. In other words, it is attraction per unit volume and is a constant for a particular real gas.

Introducing these corrections, the general gas equation is modified.

$$\left(P + \frac{a}{V^2} \right)(V - b) = RT \qquad \ldots \ldots \text{(3)}$$

For 'n' moles of a gas,

$$\left(P + \frac{a\, n^2}{V^2} \right)(V - nb) = nRT \qquad \ldots \ldots \text{(4)}$$

'a' and 'b' are called Van der Waal's constants.

1.4.3 Nature of Van der Waal's constants:

These constants are the quantitative measurement of non-ideality of the gases. They are usually determined experimentally by measuring the deviation from the real gas equation, under suitable conditions of temperature and pressures i.e., those conditions when the effects of molecular volume and mutual attractions predominate.

The values of 'a' and 'b', depend upon the nature of the gas and the units of volume and temperature. Table (3)

Units of 'a' and 'b':

The units of Van der Waal's constant are derived as follows.

Since, $P' = \dfrac{a\, n^2}{V^2}$

$$a = \frac{P'V^2}{n^2} = \frac{atm\,(dm^3)^2}{mol^2} = dm^6\, atm\, mol^{-2}$$

In S.I. units

$$a = \frac{P'V^2}{n^2} = \frac{N\,m^{-2} \times (m^3)^2}{mol^2} = \frac{N\,m^4}{mol^{-2}} = N\,m^4\, mol^{-2}$$

'b' has the units of volume mol^{-1} so, it may be expressed as $dm^3\, mol^{-1}$ or $m^3\, mol^{-1}$.

Table (2). Van der Waal's constants alongwith their units

Gases	a $dm^6 - atm\, mol^{-2}$	a $Nm^4\, mol^{-2}$	b $dm^3\, mol^{-1}$	b $m^3\, mol^{-1}$
H_2	0.244	24.72×10^{-2}	0.02661	26.61×10^{-6}
He	0.034	34.5×10^{-3}	0.02370	23.70×10^{-6}
O_2	1.360	138×10^{-2}	0.03180	31.80×10^{-6}
N_2	1.390	141×10^{-2}	0.03913	39.13×10^{-6}
CO_2	3.592	346×10^{-2}	0.04267	42.67×10^{-6}
NH_3	2.250	422×10^{-2}	0.03710	37.10×10^{-6}
CH_4	2.250	228×10^{-2}	0.04280	42.80×10^{-6}

Interconversion of units:

$$dm^3\ mol^{-1} = 10^{-3} m^3 mol^{-1}$$

$$dm^6\ atm\ mol^{-2} = 10^{-6} m^6 \times 101325\ Nm^{-2} mol^{-2}$$

$$= 1.01325 \times 10^{-1}\ Nm^4\ mol^{-2}$$

EXAMPLE (5)

Two moles of NH_3 were found to occupy a volume of 5 dm^3 at 27°C. Calculate pressure,

(i) If gas behaves ideally

(ii) Gas is real and follows Van der Waal's equation.

(a = 4.17 atm dm^6 mol^{-2}, b = 0.0371 dm^3 mol^{-1})

SOLUTION:

Volume = 5 dm^3,   T = 27°C + 273 = 300K   n = 2 moles

(i) The ideal gas obeys general gas equation

Since,

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

where R = 0.082 dm^3 atm K^{-1} mol^{-1}

Putting values

$$P = \frac{2\ moles \times 0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1} \times 300\ K}{5\ dm^3}$$

$$= 9.852\ atm.$$

(ii) Using Van der Waal's equation by considering that the gas is real

Since

$$\left[P + \frac{an^2}{V^2}\right](V - nb) = nRT$$

Rearranging the equation

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Substituting the values, we get

$$P = \frac{2 \times 0.0821 \times 300}{5 - 2 \times 0.0371} - \frac{4.17 \times (2)^2}{(5)^2}$$

$$= 9.98 - 0.67 = \boxed{9.31\ atm.} \quad \text{Ans.}$$

Ideal pressure is greater than pressure of the gas when it is non-ideal. In non-id gases the molecules have forces of attractions and the pressure is less.

1.4.4   Validity of Van der Waal's equation:

While we have discussed the non-polar behaviour of gases by graphical explanation was noticed that some of the gases have lower values of $\frac{PV}{RT}$ = Z, than expectations at

pressures. At high pressures the values of $\frac{PV}{RT} = Z$ increases too much. We have to justify these trends of gases.

For this purpose, we change the shape of Van der Waal's equation.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2} \qquad \cdots\cdots (5)$$

(i)   **At low pressure:**

When the pressure is smaller then, volume will be larger. Hence, the term 'Pb' and '$\frac{ab}{V^2}$' in equation (5) may be neglected in composition to '$\frac{a}{V}$'. Actually '$\frac{a}{V}$' represents the effect of attractions between the molecules.

Hence, equation (5) becomes,

$$PV = RT - \frac{a}{V}$$

Divide this equation by 'RT' on both sides

$$\frac{PV}{RT} = \frac{RT}{RT} - \left(\frac{a}{RTV}\right)$$

$$\frac{PV}{RT} = 1 - \left(\frac{a}{RTV}\right) \qquad \cdots\cdots (6)$$

'$\frac{PV}{RT}$' is also called compressibility factor and is denoted by Z.

Hence $Z = 1 - \frac{a}{RTV} \qquad \cdots\cdots (7)$

It means, at low pressures the compressibility factor is less than unity. It explains that, the graphs of N_2 and CO_2 lie below the ideal curve. When the pressure is increased, 'V' decreases and the value of 'Z' increases. It means that the curve should show the upward trend.

(ii)   **At high pressure:**

When the pressure is high then 'V' is small. In this case both the terms '$\frac{a}{V}$' and '$\frac{ab}{V^2}$' can be ignored,

Equation (5) is reduced to the following equation.

$$PV = RT + Pb$$

Dividing this equation with 'RT' on both sides,

$$\frac{PV}{RT} = \frac{RT}{RT} + \frac{Pb}{RT} = 1 + \frac{Pb}{RT}$$

$$Z = 1 + \frac{Pb}{RT} \qquad \cdots\cdots (8)$$

It means that at high pressure 'Z' is greater than 1 and so the graph between 'Z' and 'p' lies above the ideal gas curve. When the pressure is increased the factor $\frac{Pb}{RT}$ increases further and 'Z' becomes greater and greater.

1.5.0 CRITICAL PHENOMENON OF GASES

Boyle's law is for ideal gases. The graphs which are plotted between 'P' and 'V' at constant temperature are called isotherms. Isotherms are the parabolic curves and these curves go away from the axis, when they are plotted at higher temperature for a gas.

The idea of the study of critical phenomenon of gases was stated by Andrew (1869). He studied the isotherms of CO_2 at different temperatures. The isotherms are shown in the diagram (6) and they are drawn at 50°C, 40°C, 31.1°C, 21.5°C and 13.1°C. The graphs at 50°C and 40°C show that gas is never liquefied even at a very high pressures.
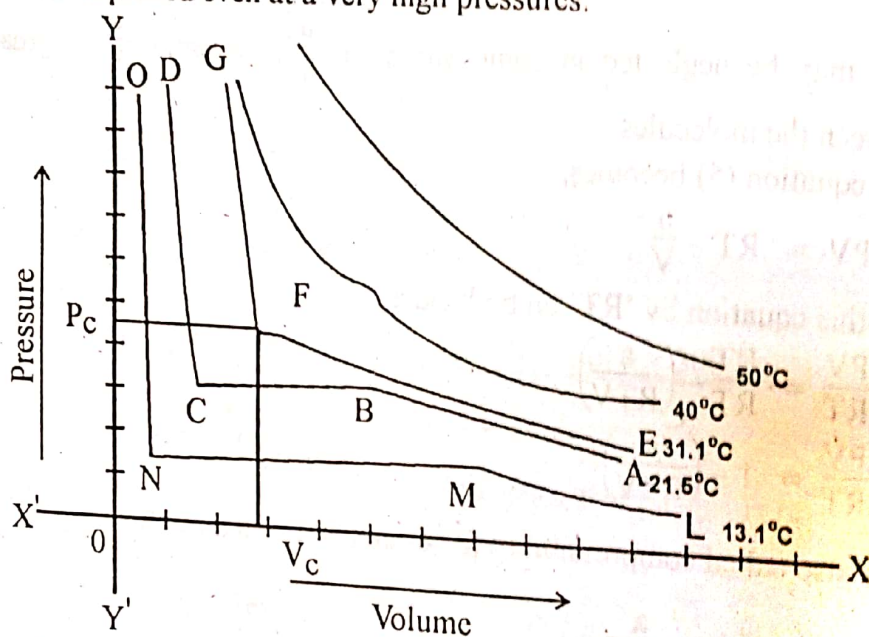

Fig. (6) Isotherms of one mole of CO_2 at various temperatures and idea of critical temperature of gases.

Anyhow, when temperature is 31.1°C, then the isotherm EFG is obtained and the CO_2 gas becomes liquid at the point F. If the temperature of CO_2 is maintained above this temperature, then liquefaction never happens for CO_2. Hence 31.1°C is called critical temperature of CO_2. It is that temperature for a gas above which the gas can never be liquefied, how much the pressure is applied. It is denoted by 'T$_c$'.

The minimum pressure required to liquify a gas at its critical temperature is called critical pressure. It is denoted by 'P$_c$'.

The volume occupied by one mole of a gas at its critical temperature and critical pressure is called critical volume. It is denoted by 'V$_c$'.

'P$_c$', 'V$_c$', and 'T$_c$', of a gas are called the critical constants. The point F is called critical point of CO_2 and the isotherm EFG is called critical isotherm.

The main conclusions which can be drawn from the above diagram are as follows.

(i)   When the temperature of CO_2 is reasonably above the critical temperature, the smooth hyperbolic curves are obtained, as we get for other ideal gases.

(ii)   The isotherm in the range of 32.5--35.5°C, do not obey the Boyle's law and smooth isotherms are not obtained.

(iii) When the temperature is maintained at 31.1°C for one mole of CO_2, then a very small horizontal portion is developed near the point F. After that, it becomes parallel to the pressure axis.

(iv)   The isotherm at 31.1°C, shows that CO_2 has become liquid at the point 'F' and if the temperature is more than 31.1°C, then there is no chance for such types of a curve.

(v)   Isotherm at 21.5°C, shows a horizontal portion. For this horizontal portion, vapours and liquid CO_2 exists in equilibrium. After the point 'C' the curve becomes parallel to the pressure axis. It means that at this temperature, low pressure than the critical pressure is required to liquify CO_2.

(vi)   The isotherm at 13.1°C has horizontal portion even longer than that at 25.5°C. It means that, even low pressure is required to liquify the gas at 13.1°C.

(vii) Closer the temperature to the critical temperature, shorter the horizontal portion of the curve and when the temperature reaches 31.1°C. then horizontal portion becomes a single point 'F'.

(viii) The isotherm below critical temperature have three portions, the right portion is for gaseous CO_2, middle is for both phases and left is for liquid phase.

1.5.1 Application of Van der Waal's equation to critical phenomenon:

In order to see, that whether the Van der Waal's equation can explain the isotherm of CO_2 or not, we should convert the Van der Waal's equation to a cubic equation in V.

$$\left(P + \frac{a}{V^2} \right)(V - b) = RT \qquad \cdots \cdots (1)$$

Open the brackets on L.H.S.

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

Multiplying by 'V²' and dividing by 'P' and rearranging we get

$$V^3 - \frac{RTV^2}{P} - bV^2 + \frac{aV}{P} - \frac{ab}{P} = 0$$

or

$$V^3 - \left(\frac{RT}{P} + b \right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \qquad \cdots \cdots (2)$$

Equation (2) is another form of Van der Waal's equation (1). This is cubic equation in 'V'. If we put the values of 'R', 'P', 'T', 'a' and 'b', then we should get three values of 'V' or three roots of 'V'. There are two possibilities.

(i)   All the three roots are real.

(ii)   One root is real and two are imaginary.

When we are above the critical temperature, then only one of these three roots is real, because there is only one volume for each pressure at constant temperature.

When we apply this equation (2) on the isotherm below critical temperature, then only two roots are real and third is missing.

Anyway, when theoretical graphs are plotted, then the horizontal portion of the curve develops the wavy shape and we can get three real roots Fig. (7). For value at given temperature and pressure, the three volumes of V at $13.1°C$ are widely separated, while three values of V at $25.5°C$ are closer to each other.

When we plot the theoretical isotherm of CO_2, at temperatures lower than $31.1°C$, then following diagram (7) is obtained.
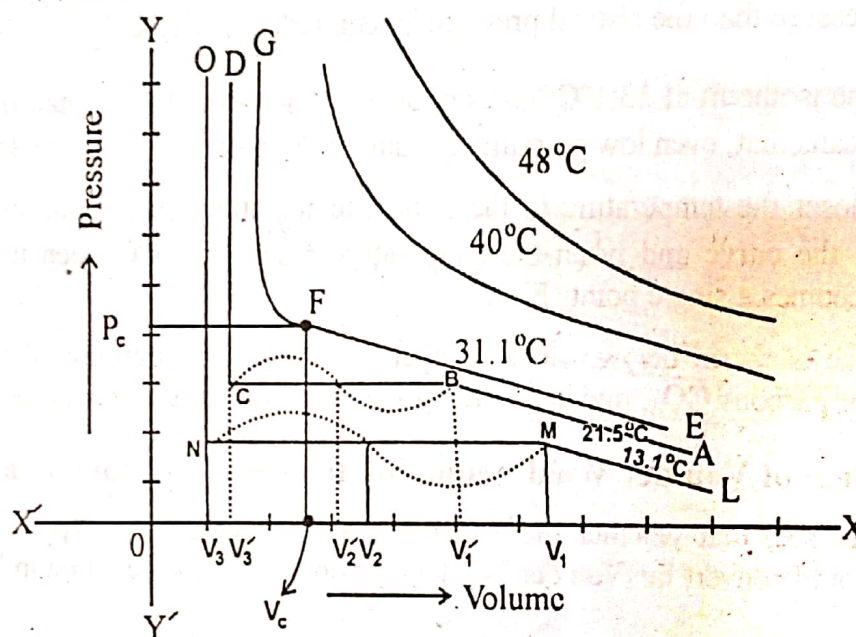

Fig. (7) *Comparison of isotherms of CO_2 above and below critical temperature.*

It means that when the temperature is increased in the equation (2), then the three real roots start coming close to each other and merge into a single point at F. The volume so obtained is a critical volume, denoted by V_c.

$$V = V_c$$

$$V - V_c = 0$$

Taking the cube of above equation,

$$(V - V_c)^3 = 0$$

or $$V^3 - 3V_c \cdot V^2 + 3V_c^2 \cdot V - V_c^3 = 0 \qquad \cdots (3)$$

It means that the equation (2) and (3) should be identical. When equation (2) is applied at point F, then all the three roots become real for same value of volume. Now fit equation (2) at critical stage, then

$$V^3 - \left(\frac{RT_c}{T_c} + b\right)V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \qquad \cdots\cdots (4)$$

Comparing equation (3) and (4), and equating the co-efficients of like powers of 'V', we get the following three expressions.

$$3V_c = \frac{RT_c}{P_c} + b \qquad \cdots\cdots (5)$$

$$3V^2_c = \frac{a}{P_c} \qquad \cdots\cdots (6)$$

$$V^3_c = \frac{ab}{P_c} \qquad \cdots\cdots (7)$$

In order to get the values of 'Pc', 'Vc' and 'Tc', we have to solve equation (5), (6) and (7) simultaneously.

Divide equation (7) by equation (6)

$$\frac{V_c^3}{3V_c^2} = \frac{ab/Pc}{a/Pc}$$

$$\frac{V_c}{3} = b$$

$$V_c = 3b \qquad \cdots\cdots (8)$$

Put the value of V for equation (8) into equation (6)

$$3(3b)^2 = \frac{a}{Pc}$$

$$Pc = \frac{a}{27b^2} \qquad \cdots\cdots (9)$$

Putting equation (8) and (9) in equation (5)

$$3(3b) = \frac{RTc}{\dfrac{a}{27b^2}} + b$$

$$9b - b = \frac{RTc}{\dfrac{a}{27b^2}} \quad , \qquad 8b = \frac{RTc}{\dfrac{a}{27b^2}}$$

$$RTc = \frac{a}{27b^2} 8b = \frac{8a}{27b}$$

$$Tc = \frac{8a}{27Rb} \qquad \cdots\cdots (10)$$

Now, determine the valves of 'a' and 'b',

Since, $V_c = 3b$

So, $\boxed{b = \dfrac{V_c}{3}}$ ...... (11)

...... (6)

Since $\dfrac{a}{P_c} = 3V^2_c$

...... (12)

So $\boxed{a = 3P_c V_c^2}$

We know that for one mole of an ideal gas

$$PV = RT$$

$\therefore$ $R = \dfrac{PV}{T}$

Now find the value of $\dfrac{P_c V_c}{T_c}$. For that, put the values from equations (8), (9) and (10).

$$\frac{P_c V_c}{T_c} = \frac{\dfrac{a}{27b^2} \cdot 3b}{\dfrac{8a}{27Rb}}$$

$$\frac{P_c V_c}{T_c} = \frac{a}{27b^2} \cdot 3b \times \frac{27Rb}{8a}$$

$\boxed{\dfrac{P_c V_c}{T_c} = \dfrac{3}{8} R}$ ...... (13)

EXAMPLE (6)

You are provided with CO_2. Calculate the critical volume, critical temperature and the critical pressure for this gas. The value of critical constants for CO_2 are, $a = 3.61$ atm dm^6 mol^{-2}, and $b = 4.27 \times 10^{-2}$ dm^3 mol^{-1}.

SOLUTION:

DATA:

$a = 3.61$ dm^6 atm mol^{-2}

$b = 4.27 \times 10^{-2}$ dm^3 mol^{-1}

Calculation of critical volume

Since $V_c = 3b$

Putting value of 'b'

$V_c = 3 \times 4.27 \times 10^{-2}$ dm^3 mol^{-1}

$V_c = 12.81 \times 10^{-2}$ dm^3 mol^{-1}

It means that one mole of CO_2 at critical stage occupies a volume of 0.1281 dm^3.

Calculation of critical pressure

Since $P_c = \dfrac{a}{27\,b^2}$

Putting the values of a, b

$$P_c = \frac{3.61\ \text{atm dm}^6\ \text{mol}^{-2}}{27(4.27 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1})^2}$$

$$P_c = \frac{3.61\ \text{atm dm}^6\ \text{mol}^{-2}}{0.0492\ \text{dm}^6\ \text{mol}^{-2}} = 73.33\ \text{atm.}$$

Calculation of critical temperature (T_c)

Since, $T_c = \dfrac{8a}{27\,Rb}$

Putting the values of a, b and R,

$$T_c = \frac{8 \times 3.61\ \text{atm dm}^6\ \text{mol}^2}{27 \times 0.0821\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1} \times 4.27 \times 10^{-2}\ \text{dm}^3 \cdot \text{mol}^{-1}}$$

$$T_c = \boxed{305.1\ \text{K}} \qquad \text{Ans.}$$

EXAMPLE (7)

The values of critical temperature (T_C) and pressure (P_C) of chlorine are 419 K and 9.474×10^6 Nm^{-2}. Calculate the values of Van der Waal's constants 'a' and 'b'. (R = 8.314 JK^{-1} mol^{-1}).

SOLUTION:

DATA:

$T_C = 419\ \text{K}$

$P_C = 9.74 \times 10^6\ \text{Nm}^{-2}$

$R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$

Since, $a = \dfrac{27\,R^2 T_C^2}{64\,P_C}$

Putting values,

$$a = \frac{27 \times (8.314)^2\ \text{J}^2\ \text{K}^{-2}\ \text{mol}^{-2} \times (419)^2\ \text{K}^2}{64 \times 9.474 \times 10^6\ \text{Nm}^{-2}}$$

$$a = \boxed{0.54\ \text{Nm}^4\ \text{mol}^{-2}} \qquad \text{Ans.}$$

Since, $b = \dfrac{R T_C}{8\,P_C}$

Putting values,

$$b = \frac{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 419\ \text{K}}{8 \times 9.474 \times 10^6\ \text{Nm}^{-2}}$$

$$b = \boxed{4.59 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}} \qquad \text{Ans.}$$

Since, $\boxed{1\ \text{J} = \text{Nm} = 0.0459\ \text{dm}^3\ \text{mol}^{-1}}$

LIQUIDS

2.6.0 STRUCUTRE OF LIQUIDS

A liquid may be regarded as a continuation of a gas phase into the region of small volumes and very high molecular attractions. Our present knowledge about the nature of the liquid state is still very incomplete. There are two main theories of liquid structure.

One theory considers liquid as an imperfact gas. This is supported by the fact that above the critical point there is no distinction at all between the liquid and a gas the so-called fluid state of matter exists.

The second view point about the structure of liquid considers it similar to a crystal except that the well ordered arrangement of the liquid extended over to only five or six molecular diameter. This is often referred to as short-range order and long-range disorder. It is more plausible model since near the melting point, the densities of crystal and liquid lie close together. Whatever order exists in a liquid structure, it is continuously changing because of the thermal motions of individual molecules. The properties of liquids are determined by a time average of a large number of different arrangements.

Now, we are going to discuss some important physical properties like, viscosity, surface tension and refractive index. 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.

1.6.1 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

1.6.2 Properties of liquids:

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

1.7.0 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 (10) makes the idea clear.
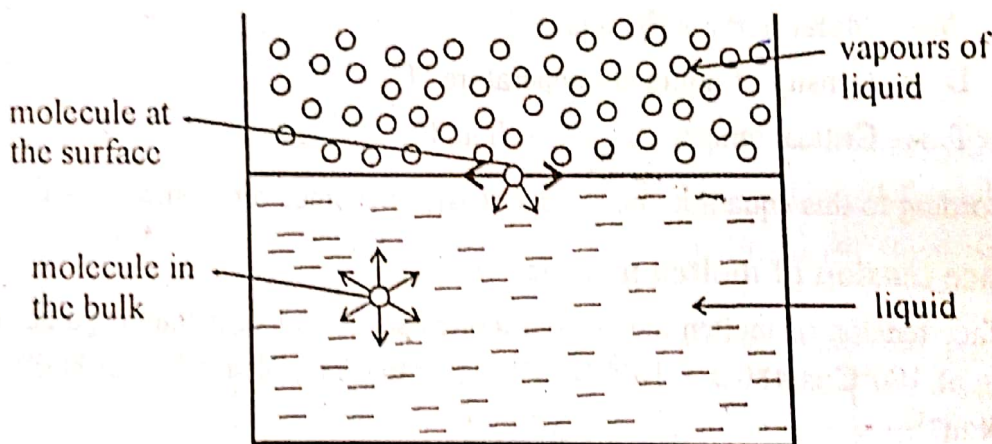

Fig. (10). *The attractive forces which are experienced by the molecules at the surface and inside the molecules.*

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}.

1.7.1 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 (4). Surface tension of liquids at different temperatures
$(N\ m^{-1} \times 10^{+3} = \text{milli } N\ m^{-1})$ $(1\ \text{milli } Nm^{-1} = 1\ \text{dyne cm}^{-1})$

Temp (°C)	H_2O	C_2H_5OH	$C_6H_5 - NO_2$	CCl_4	C_6H_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 $1000 = 10^{13}$)

The comparison shows that surface tension of H_2O has greater values than other liquids various temperatures.

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

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

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 $T = T_C$.

1.7.2 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 $480.3 \times 10^{-3}\ N\ m^{-1}$, while that of molten silver at 800°C has a value of $800 \times 10^{-3}\ N\ m^{-1}$.

1.7.3 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.

1.7.4 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 (1) shows that how the liquid is compelled to enter the capillary tube from the lower side.
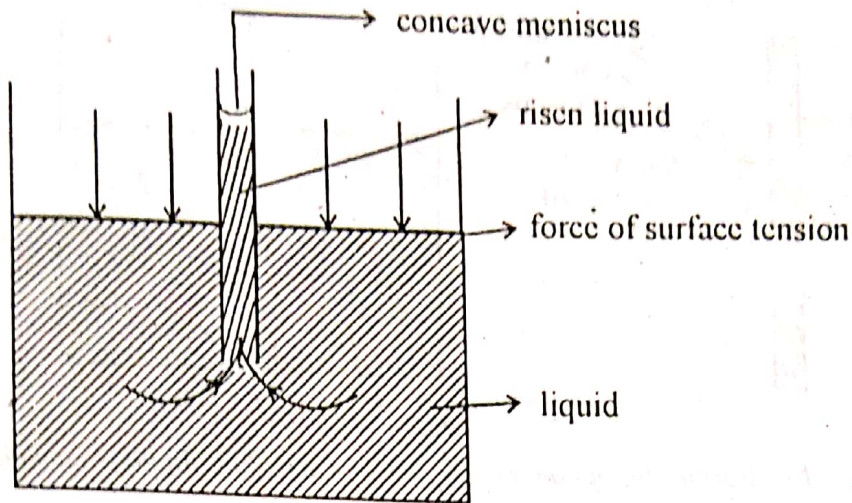
Fig. (11) How the liquid is compelled to rise in the capillary tube.

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.

1.7.5 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 (0) is inside the liquid between the solid. The solid-liquid interface as shown in the following diagram (12). The contact angle is less than 90°.
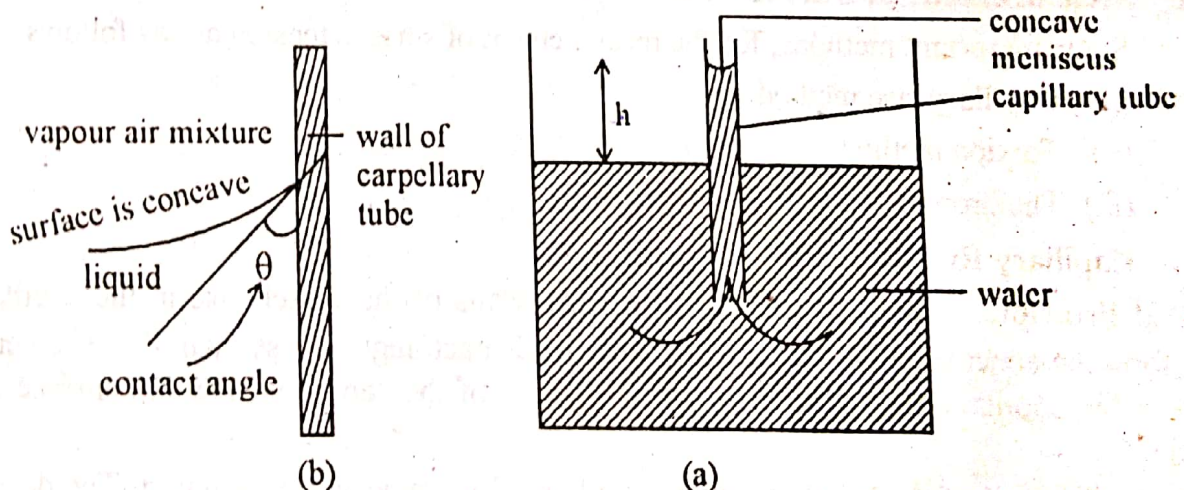

Fig. (12) Formation of concave meniscus for a rising liquids like water.

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 (13).
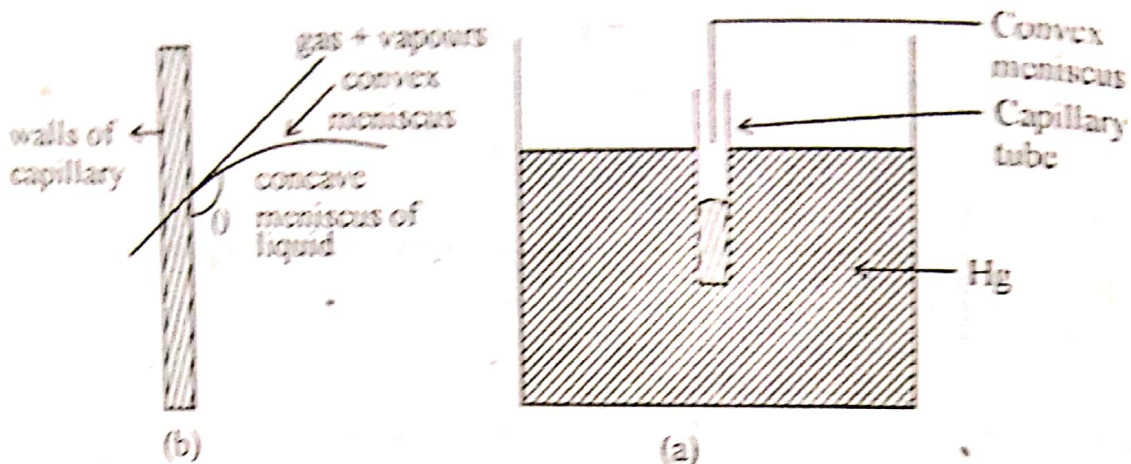
Fig. (13) Formation of convex meniscus for a falling liquids like mercury.

1.7.6 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.

1.7.7 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.

1.7.8 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 (14) makes the idea clear.
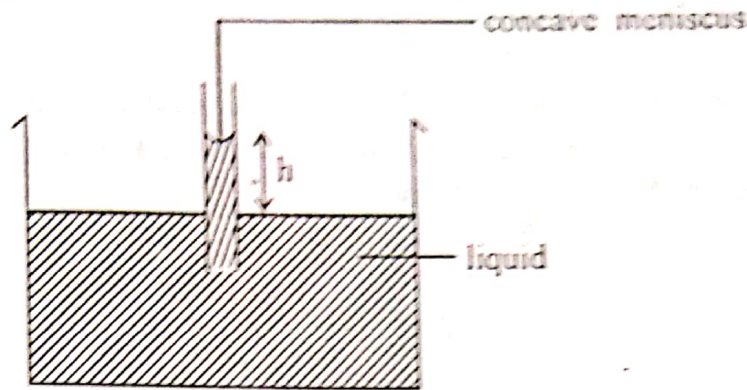
Fig. (14) Capillary rise method for surface tension measurement.

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

$$\text{Radius of capillary tube} = r$$
$$\text{Base area of tube} = \pi r^2$$
$$\text{Height of liquid} = h$$

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

Density of liquid $= d$

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

So,

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

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

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

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

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

If the radius of the capillary tube is very small, then the **contact angle '0'** approaches to zero.

$$\cos(0°) = 1$$

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

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^{-3} 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:

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

$$h = 5 \times 10^{-3} \, m$$

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

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

Since

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

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

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

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

(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 (15), 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
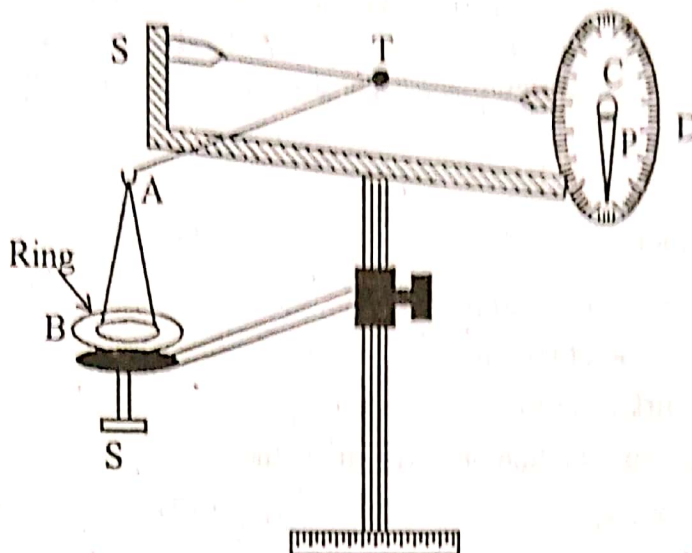
r = radius of platinum ring

Fig. (15) 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 (16).
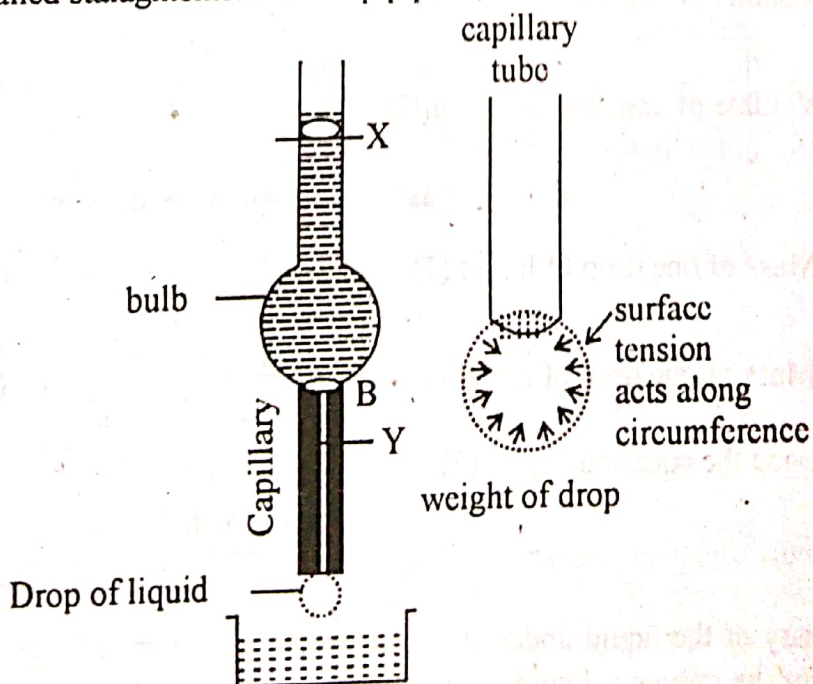

Fig. (16) Stalagmometer to measure the surface tension of a liquid.

Around twenty drops of the given liquid are received from the drop pipette in a weigh bottle. In this way, the weight of one drop in calculated. Then the stalagmometer is cleaned dried and filled with a reference liquid say water and weight of one drop of water is calculated 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 o 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 tensio to be measured. The number of drops are counted till the liquid flows up to the mark Similarly, the number of drops of the reference liquid say water are counted from mark 'X '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,

$$\text{mass} = \text{volume} \times \text{density}$$

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

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

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 va 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)

$$d_{(w)} = 1 \times 10^3 \text{ kg m}^{-3}$$

$$\gamma_w = 7.2 \times 10^{-2} \text{ Nm}^{-1}$$

$$\gamma_l = ?$$

Formula used

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

Putting values

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

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

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

1.8.0 THE PARACHOR

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

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

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

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

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

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

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

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 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,

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

1.8.1 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 (5) 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

## 1.8.2 Applications of parachor for structure verification:

In order to verify the structure of the compound, we should determine the parachor in laboratory by measuring the surface tension and putting the value of molar volume in 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 keeping in mind this structure which has been proposed.

(i)   **Structure of benzene:**

Kekule has given the structure of benzene as follows,
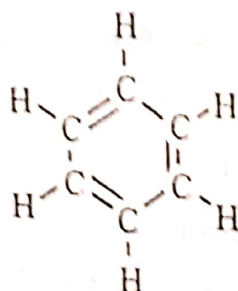
When we sum up the values of atomic parachors and structural parachors of benzene keeping in view its cyclic structure i.e. number of double and single bonds, then it comes to 206.9.

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 206.7. These two values agree with each other. So, Kekule's structure is confirmed.
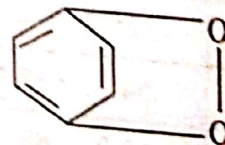
(ii)   **The Structure of quinone:**

Two possible structures have been proposed.

and

(I)   (II)
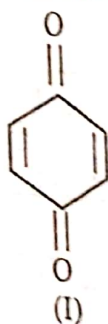
235.5   216.5

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

to

(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:

$$-N\diagdown^O_O \quad -N\diagup^O_{O} \quad -N\diagup^O_{O} \quad -N\diagup^O_O$$

(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.

$$3CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - H \longrightarrow \text{Paraldehyde}$$

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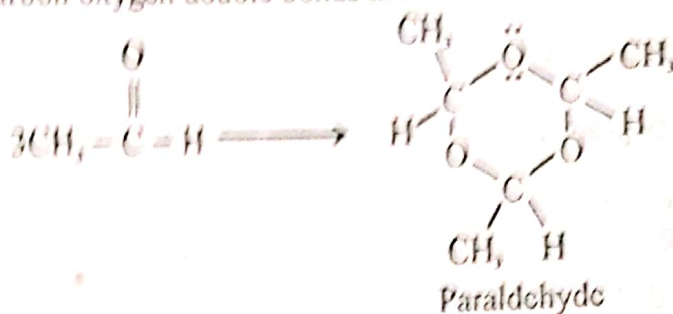
5, **Structure of positional isomers:**

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-chlorotoluene, the value is 283.6.

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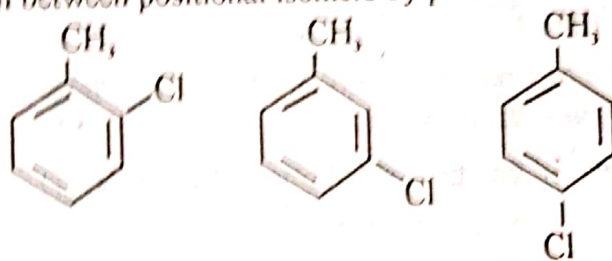
1.9.0 VISCOSITY

1.9.1 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

(17). 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.

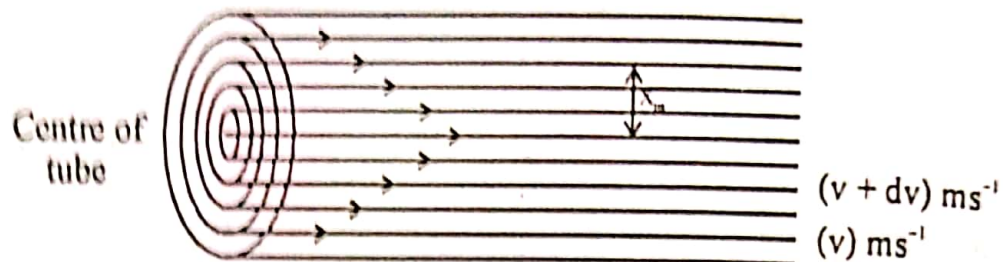When the steady flow is reached then velocity difference between any two layers becomes constant.

Centre of tube

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

(v) ms^{-1}

Fig. (17) 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.

A = Area of contact

$\dfrac{dv}{dx}$ = Velocity gradient

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

or $$F = -\eta A \dfrac{dv}{dx} \qquad \cdots\cdots (1)$$

$$\eta = -\dfrac{F}{A \cdot \dfrac{dv}{dx}} \qquad \cdots\cdots (2)$$

η = co-efficient of viscosity or simply called viscosity.

1.9.2 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)

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

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

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

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

In SI units η is in kg m^{-1} s^{-1}

1 poise = 10^{-1} kg m^{-1} s^{-1} = 0.1 kg m^{-1} 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."

$$1 \text{ centipoise} = 10^{-2} \text{ poise}$$
$$1 \text{ millipoise} = 10^{-3} \text{ poise}$$

Fluidity:

"Fluidity is the reciprocal of viscosity."

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

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

1.9.3 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.

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

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)

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

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

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. (18) 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.
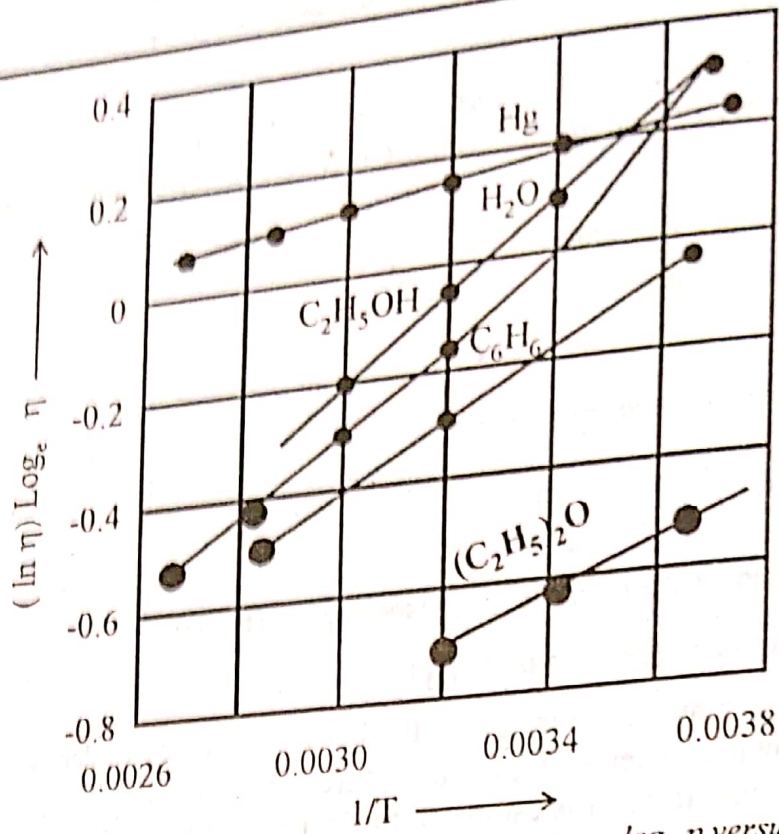
Fig. (18) The dependence of viscosity on temperature $\log_e \eta$ versus $1/T$.

Viscosities of some important liquids:

Table (6): 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

1.9.4 Measurement of viscosity:

General Principle:

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

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

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.

1.9.5 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."*

1.9.6 Measurement of relative viscosity:

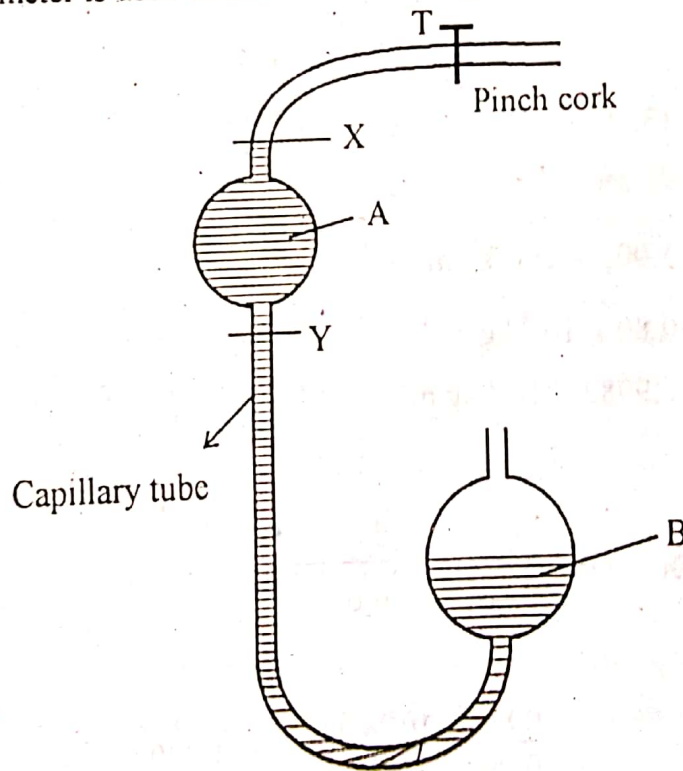Ostwald's viscometer is used as shown in following diagram (19).

Fig. (19) 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 factors.

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

η_1 = viscosity of liquid

η_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 (4)

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:

$$t_{alc} = 135 \text{ sec}$$

$$t_{H_2O} = 90 \text{ sec}$$

$$\eta_{H_2O} = 1.005 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$$

$$d_{alc} = 0.80 \times 10^{-3} \text{ kg m}^{-3}$$

$$d_{H_2O} = 0.9982 \times 10^{-3} \text{ kg m}^{-3}$$

$$\eta_{alcc} = ?$$

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

Putting values

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

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

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

1.9.7 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.

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

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.

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

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

Table (7) Values of $\dfrac{d}{M} \times \eta \times 10^6$

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 (8) 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	— CH$_2$	23.6
	(in HCl)	9.7	— C$_6$H$_5$	100.7
	(in HBr)	12.6	$-C\diagdown{\!}^{O}_{O}$	36.0
	(in HI)	15.0	— NH$_2$	20.6
Chlorine		27.3	> NH	13.6
Bromine		35.8	CN	33.0
Iodine		47.6		
Nitrogen		6.6		

1.9.8 Measurement of molar mass of polymer:

Molar masses of polymers are very high. It depends upon the reaction conditions wheth the molar mass of the polymer is high or low. The measurement of viscosity of solutions 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 polym 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 $c \to 0$. The value of η_{sp}/c having the value at that stage is called $\eta_{Intrinsic}$.

1.10.0 REFRACTIVE INDEX

1.10.1 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. (20)
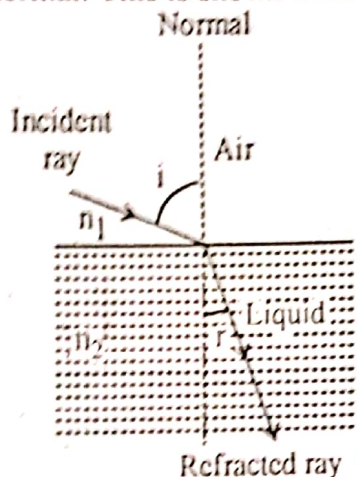

Fig. (20) Refraction of light.

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. (21)
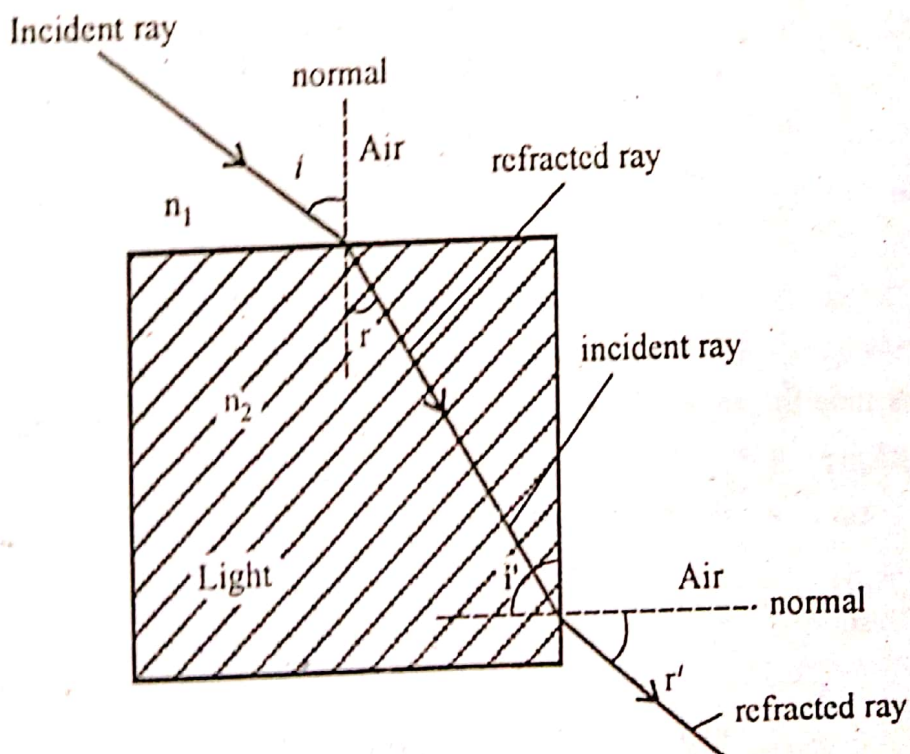

Fig. (21) How the image in displaced due to refraction.

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

1.10.2 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 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.

1.10.3 Critical angle of refraction:

When the angle of incidence increases, then the angle of refraction also increases. W the angle of incidence is equal to $90°$, then the 'r' approaches to its maximum value as show the following diagram (22).
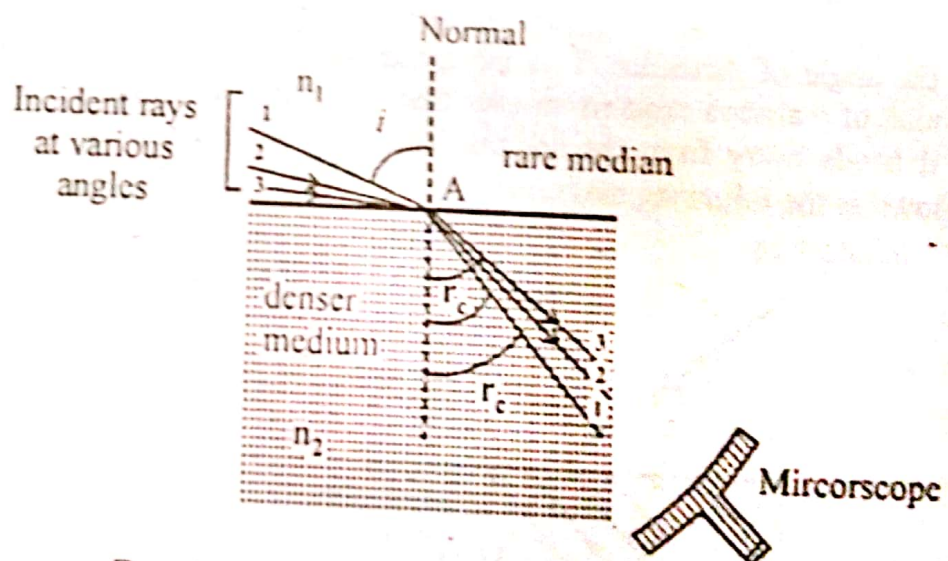

Fig. (22) The principle of critical angle of refraction.

At this time the angle of refraction is called critical angle of refraction, denoted by 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 $90°$.

1.10.4 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 refactometer:

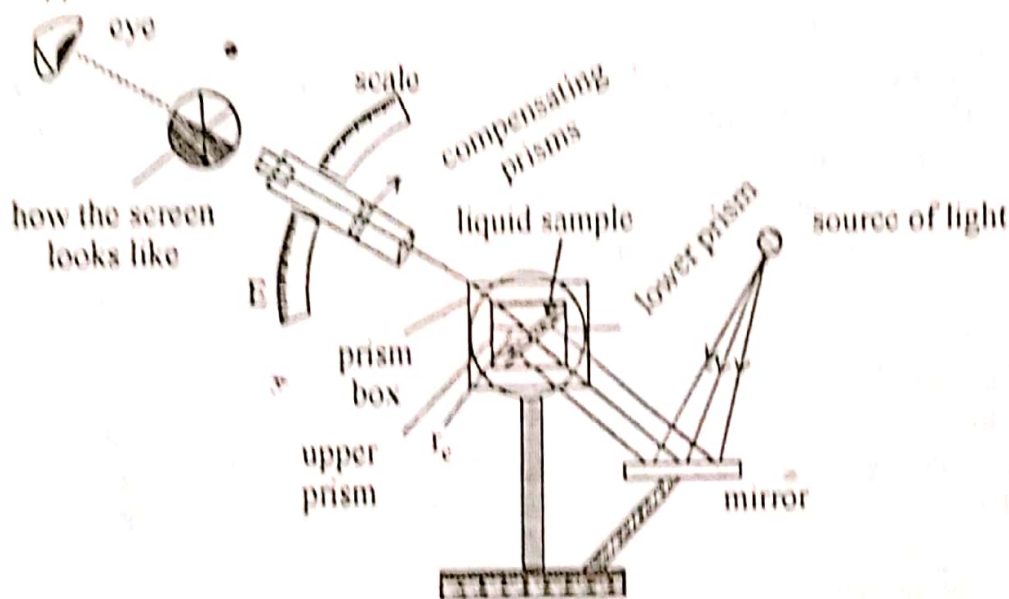This apparatus is as shown in the following diagram. (23)

Fig. (23) 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 hypotenuse 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. Follow arrangement (24) is helpful to understand the principle and working of Pulfrich refractometer.
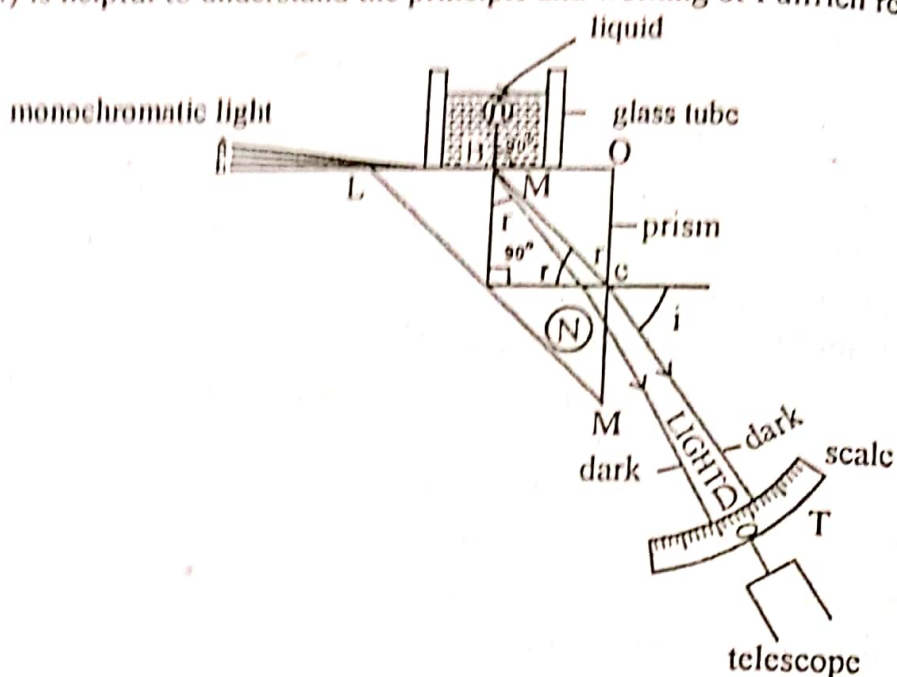

Fig. (24) The optical system of Pulfrich refractometer.

This refractometer has right angled glass prism, L M O. A glass cell is attached on the 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 the 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 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, $\sin r = \dfrac{n}{N}$ ...... (1)

The above diagram also shows that,

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

Since, $\sin (90° - r) = \cos r$

Hence, equation (2) becomes

$\dfrac{\sin i}{\cos r} = N$ ...... (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.

1.10.5 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.

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

'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.

1.10.6 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'.

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

'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.

1.10.7 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 $m^3\ kg^{-1}$

1.10.8 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 $\dfrac{M}{d}$

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

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

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 (9).

Table (9) 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}

1.10.9 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 simple, 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 (10)

Table (10), Molar refraction in $cm^3 \, mol^{-1}$ for atoms, groups and bonds.

Carbon (C)	2.418	COOH group	7.771
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

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

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

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

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

$$R_m = 0.0262 \times 10^{-3} \, m^3 \, mol^{-1}$$

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

1.10.10 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 − C − C − O
(structure diagram with H atoms)
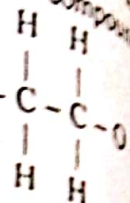
Refractive index of C_2H_5OH = 1.3611

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.

1.10.11 Molar refraction of the solution:

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

$$R_m = \frac{n^2 - 1}{n^2 + 2} \left(\frac{X_1 M_1 + X_2 M_2}{d} \right)$$

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.

1.10.12 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 double bond, then optical exaltation is also there.

The following table (11) shows the values of optical exaltation for some of the conjugated systems.

Table (11). 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	$(CH_3)_2C = CH - \overset{\overset{O}{\|}}{C} - CH = C(CH_3)_2$	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}

1.10.13 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
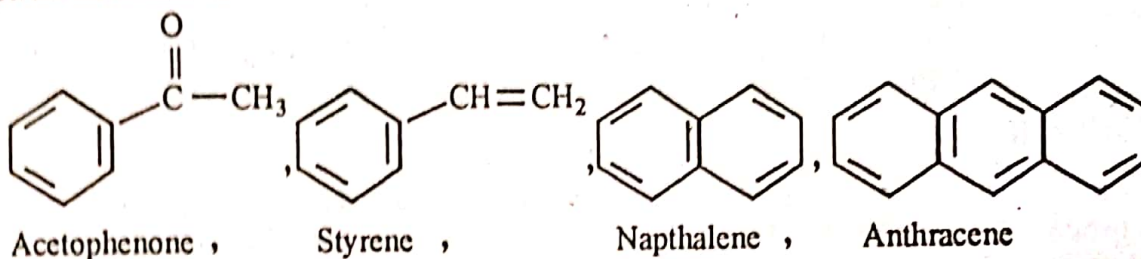
SOLIDS

1.11.0 INTRODUCTION

Those substances which are rigid, hard, have definite shape and definite volume are called solids. They can retain their shape without being confined in a vessel.

There are two types of solids.

(i)   Amorphous solids   (ii)   Crystalline solids

(i)   **Amorphous solids:**

"Those solids in which the constituent particles i.e., atoms, ions or molecules of the substances are not arranged in any regular fashion." They are not accepted as true solids.

For example, glass, pitch and the polymers of high molar masses are amorphous solids. They are also regarded as supercooled liquids of high viscosity.

(ii) Crystalline solids:

"Those solids in which the constituent particles like atoms, ions or molecules of the substance are arranged in definite geometric pattern within the solid are called crystalline solids." The substances like metals and many of the salts are crystalline in nature.

1.11.1 Space lattice:

"The regular arrangement of constituent particles i.e., atoms, ions and molecules of a crystalline substance in three dimensions is called space lattice." The following diagram (25) shows the space lattice of a hypothetical crystalline substance.
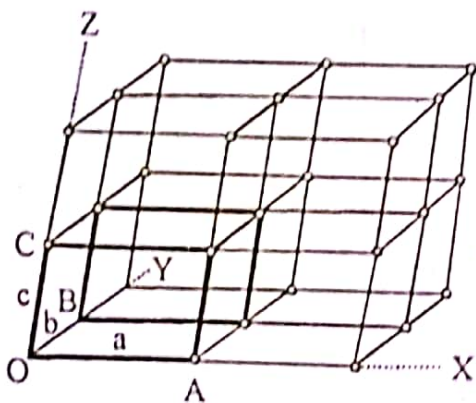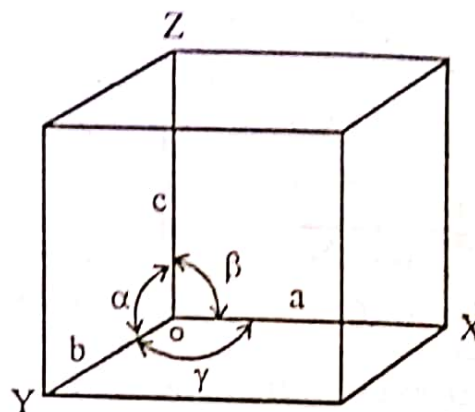

Fig. (25) Space lattice and lattice points

Fig. (26) Unit cell and unit cell dimensions

When we look at the crystal lattice, then we note that

(i) Each lattice point has the same environment as that of any other point in the lattice.

(ii) A constituent particle is to be represented by lattice point, irrespective of the fact and whether it contains the single atom or more than one atoms.

1.11.2 Unit cell:

When we picturize a crystal lattice as shown in the above diagram (26), then it is possible to select a group of lattice points. This group of lattice points repeated again and again is called the unit cell. The whole lattice can be generated by translation or stacking of these unit cells.

So, unit cell is a three dimensional group of lattice points which generate the whole lattice by translation or stacking. Fig. (2)

1.11.3 Types of unit cells:

Unit cell can be divided into four types.

(i) **Simple unit cell:** This type of unit cell is produced, when the particles are present only at the corners of the unit cell.

(ii) **Face centred unit cell:** When the particles are located at the centre of each face in addition to the corners, then it is called face centred unit cell.

(iii) **End face centred unit cell:** When the particles are located at the centers of the end face in addition to the corners, then it gives end face centred unit cell.

(iv) **Body centred unit cell:** When the particles are present at the centre of the cell in addition to the corners, then it is called body centred unit cell.

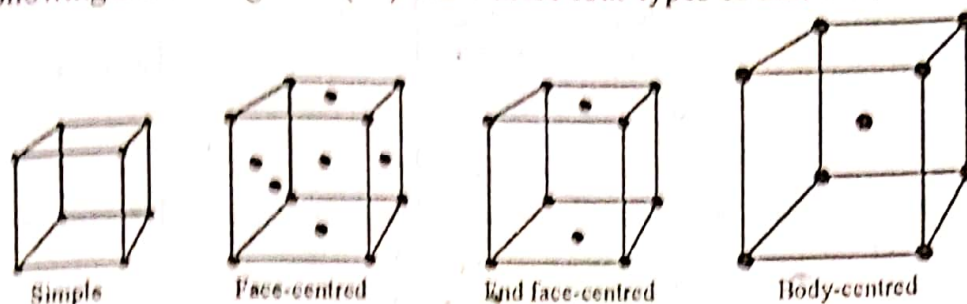The following set of diagrams (27) show these four types of unit cell.

Simple   Face-centred   End face-centred   Body-centred

Fig. (27) Types of unit cells.

1.11.4 Crystal Systems:

Each unit cell is a parallelopiped, whose interfacial angles may r may not be $90°$. The three lengths a, b, c and three interfacial angles are called unit cell dimensions. The relationship between the values of the angles and between the lengths of the axes give us seven types of crystal systems as shown in the following Table (12).

Table (12): The seven crystal systems and fourteen Bravais lattices

Systems	Bravais lattices	unit cell characteristics	characteristic symmetry elements	examples
Cubic	3 simple, body-centred, face-centred	three axes at right angles: all equal $a = b = c$ $\alpha = \beta = \gamma = 90°$	four 3-fold rotation axes (along cubic diagonals)	NaCl, ZnS, FeS$_2$, KCl, Diamond, Au, Hg, Ag, Pb,
Tetragonal	2 simple, body-centred	three axes at right angles: two are equal $a = b \neq c$ $\alpha = \beta = \gamma = 90°$	one 4-fold rotation axis	SnO$_2$, TiO$_2$, Sn, KH$_2$PO$_4$
Orthorhombic	4 simple, body-centred, face-centred, end-centred.	three axes at right angles: but all unequal $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	three mutually orthogonal 2-fold rotation axes	KNO$_3$, PbCO$_3$, BaSO$_4$, rhombic sulphur
Monoclinic	2 simple, end-centred	three axes, all unequal, two axes at right angles, third is inclined to these at an angle other than $90°$ $a \neq b \neq c$ $\alpha = \gamma = 90°$, $\beta \neq 90°$	one 2-fold rotation axis.	CaSO$_4$.2H$_2$O, Na$_2$SO$_4$.10H$_2$O , Na$_2$B$_4$O$_7$.10H$_2$O, monoclinic sulphur

The following set of diagrams (27) show these four types of unit cell.

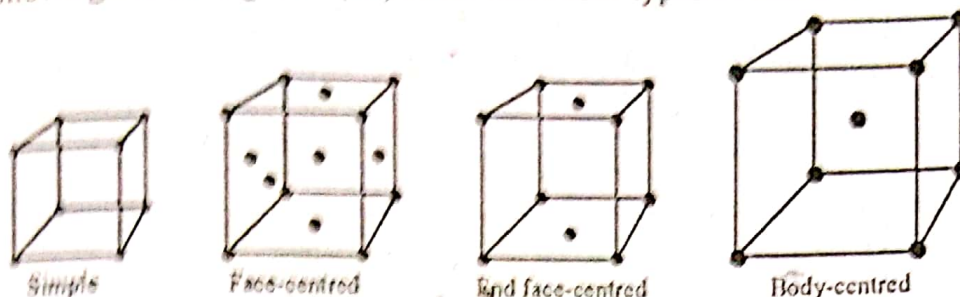Simple   Face-centred   End face-centred   Body-centred

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