GASES

Introduction:

Matter exists in three principal states i.e., gases, liquids and solids. Behaviour of gases is more simple and there is uniformity in the properties of gases. When the external conditions of temperature and pressure are changed, then the volume of the gases are affected to same extent. That is why, all the gases more or less follow the same principles and laws. These laws are given briefly as follows.

1.1.0 LAWS OF GASES

1.1.1 Boyle's law:

This law states that *"the volume of a given mass of a gas is inversely proportional to the pressure provided that the temperate remains constant."*

$$V \propto \frac{1}{P} \quad \text{(when temperature 'T' and number of moles 'n' are constant)}$$

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

$$PV = k$$

$$\text{or } P_1V_1 = P_2V_2 = P_3V_3 = k \quad \cdots\cdots (1)$$

When the 'T' and 'n' are constant.

If a graph is plotted for a gas between volume on x-axis and pressure on y-axis, then parabolic curve is obtained at constant temperature. Such curves are called isotherms. When the temperature of a gas is decreased, then the isotherms come close to the axis. Following Fig. (1) makes the idea clear.
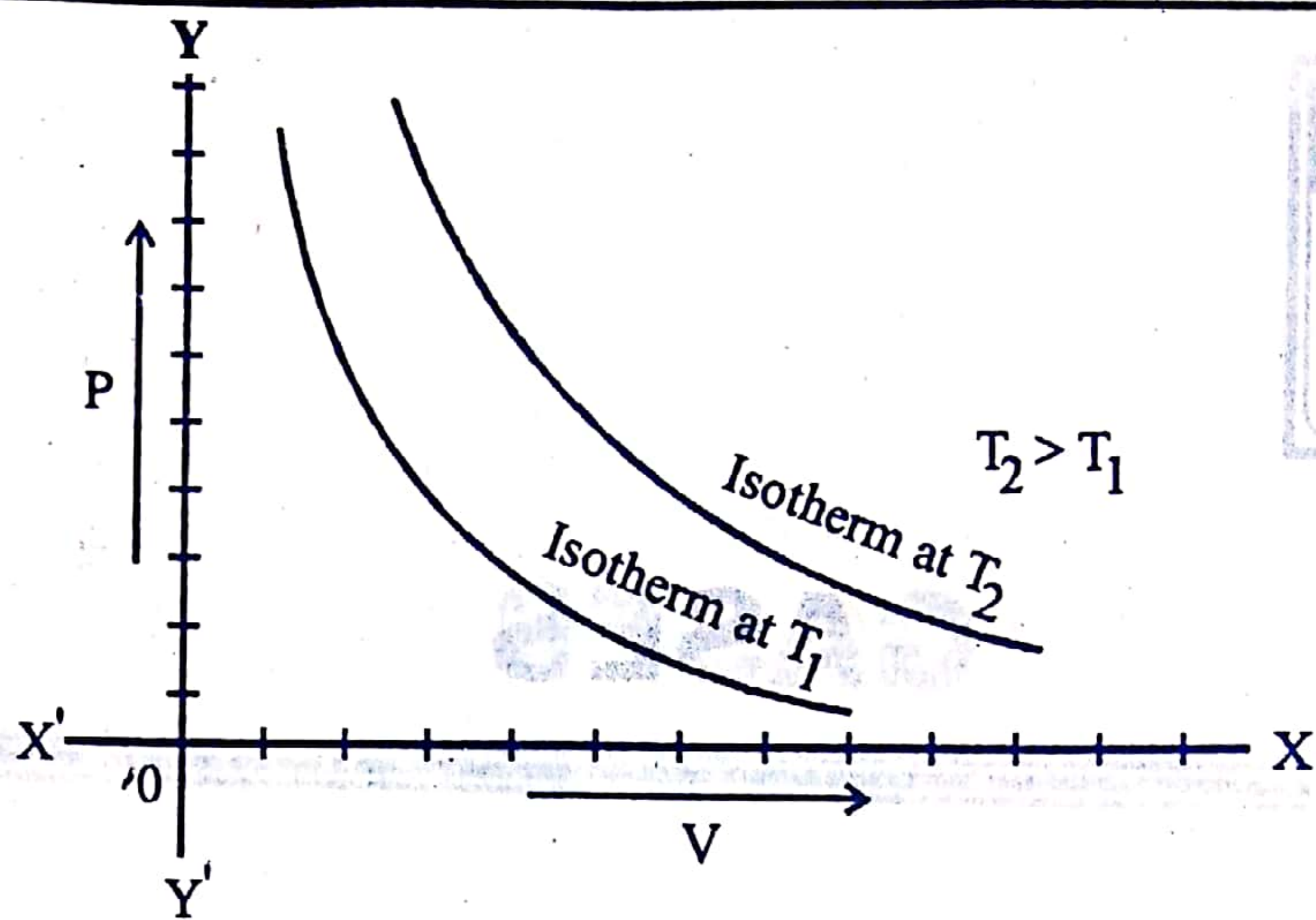
Fig. (1) Isotherms of Boyle's law.

1.1.2 Charles's law:

This law states that "the volume of a given mass of a gas increases or decreases by $\frac{1}{273}$ of its volume at 0°C, for every one degree rise or fall of temperature provided that the pressure is constant."

From this law, we get the idea of absolute zero, which starts from -273.16°C. This is the lowest temperature which is never attained. When the graph is plotted between temperature on x-axis and volume of gas on y-axis, it gives a straight line and when extrapolated meets the temperature axis at -273.16°C. Fig. (2)
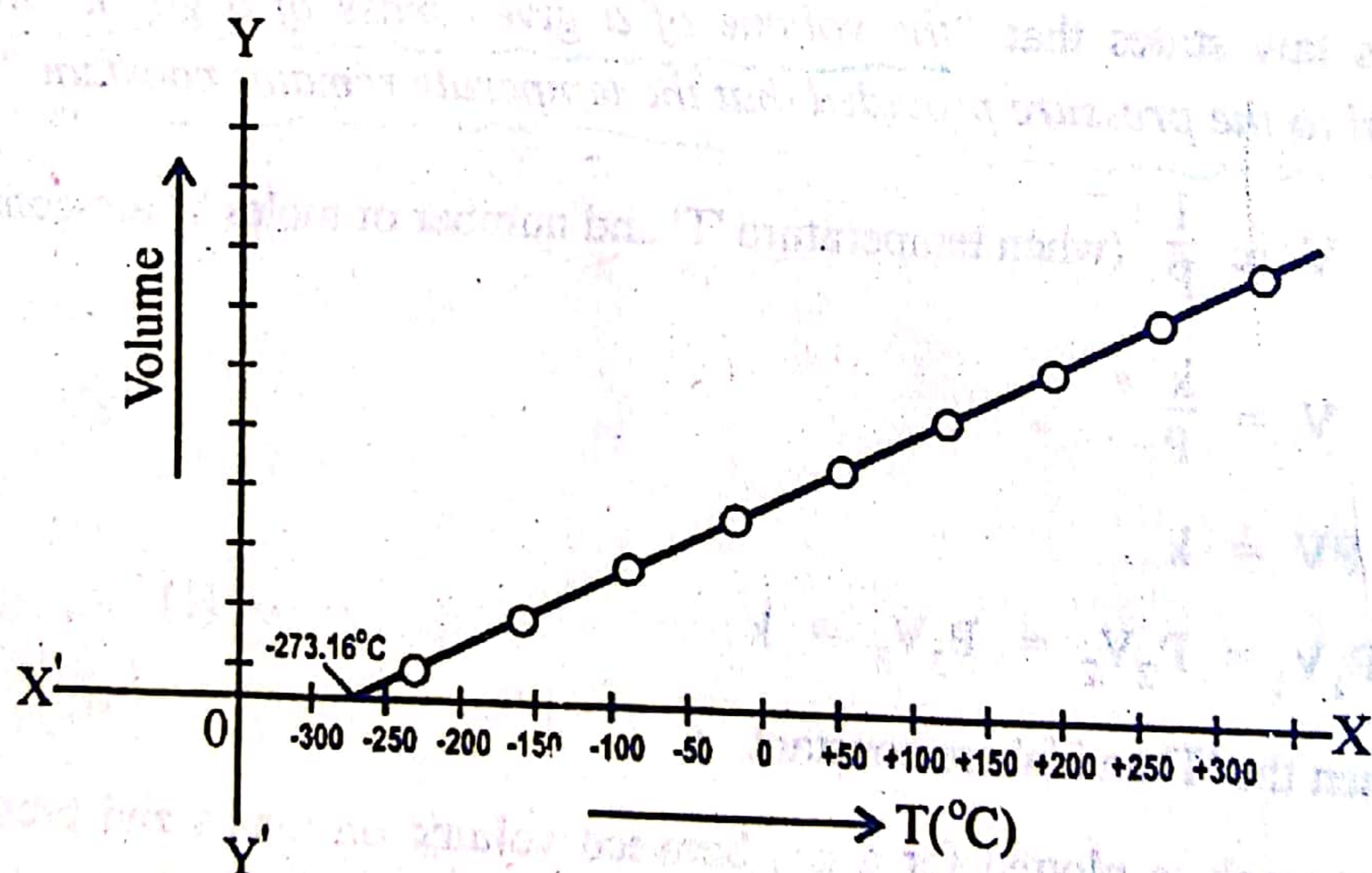

Fig. (2) Graphical explanation of absolute zero by Charles's law.

1.1.3 Combined gas law:

Keeping in view, the Boyle's law and the Charles's law, we can prove that

$$V \propto \frac{nT}{P}$$

Since $V \propto n$, $V \propto T$ and $V \propto \frac{1}{P}$

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

or $$PV = nRT \qquad \ldots\ldots (2)$$

This is a general gas equation in which 'R' is general gas constant and 'n' is the number of moles of the gas. This equation has another shape as well.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad \ldots\ldots (3)$$

or $$d = \frac{PM}{RT} \qquad \ldots\ldots (4)$$

In equation (4) 'd' is the density of the gas 'P' is pressure and 'M' is the molar mass. The density of gas is directly proportional to pressure and inversely proportional to the temperature.

Gas constant:

'R' is called universal gas constant. Its significance can be readily understood, if you examine the nature of the quantities which make its values.

Since $$PV = nRT$$

so $$R = \frac{PV}{nT}$$

or $$R = \frac{\text{pressure} \times \text{volume}}{\text{temperature} \times \text{no. of moles}}$$

Since, pressure is force per unit area

$$R = \frac{\text{force}}{\text{area}} \times \frac{\text{volume}}{\text{temperature} \times \text{no. of moles}}$$

Where $$\text{area} = (\text{length})^2$$
$$\text{volume} = (\text{length})^3$$
temperature is in kelvin

So, $$R = \frac{\text{force}}{(\text{length})^2} \times \frac{(\text{length})^3}{\text{kelvin} \times \text{no. of moles}}$$

$$= \frac{\text{force} \times \text{length}}{\text{kelvin} \times \text{no. of moles}}$$

Where Force $\times$ length = Energy or work

So, $$R = \frac{\text{Energy (work)}}{\text{kelvin} \times \text{no. of moles}} = \text{Energy. K}^{-1}.\text{mol}^{-1}$$

It means that the 'R' will be expressed in terms of energy per kelvin per mole. When we use the Avogadro's principle, then the values and units of 'R' are as follows.

Values and units of 'R':

According to Avogadro's law for gases, one mole of an ideal gas at standard temperature and pressure occupies the volume of 22.414 dm^3.

Since $R = \dfrac{PV}{nT}$ $P = 1$ atm., $V = 22.414$ dm^3

Putting values

$$R = \frac{1(\text{atm}) \times 22.414 \ (\text{dm}^3)}{1(\text{mol}) \times 273(\text{K})} = 0.082 \ \text{dm}^3 \ \text{atm} \ \text{K}^{-1} \ \text{mol}^{-1}$$

If the units of pressure and volume are taken in S.I system, then

$P = 101325$ Nm^{-2} (since 1 atm $= 101325$ Nm^{-2})

$V = 0.0224$ m^3 (Since 1 dm$^3 = 10^{-3}$ m^3)

Putting values

$$R = \frac{101325 \ \text{Nm}^{-2} \times 0.0224 \ \text{m}^3}{1 \ \text{mol} \times 273 \ \text{K}} = 8.3143 \ \text{Nm} \ \text{K}^{-1} \ \text{mol}^{-1}$$

Since   Nm = J

So, $R = 8.3143$ J.K^{-1} mol^{-1}

We know that, 1 calorie = 4.18 Joules

The value of R may be expressed in calories

$$R = \frac{8.3143}{4.18} \ \text{JK}^{-1} \ \text{mol}^{-1} = 1.987 \ \text{cal} \ \text{K}^{-1} \ \text{mol}^{-1}$$

1.1.4 Avogadro's law:

Those real gases which obey the Boyle's law and Charles's law at low pressure follow the principle of the Avogadro's law. This law states that, "equal volumes of all the gases at same temperature and pressure contain equal number of molecules."

Actually, this statement is derived from this idea that one mole of an ideal gas at standard temperature and pressure occupies the volume of 22.414 dm^3. We know that one mole of an ideal gas contains 6.02×10^{23} molecules of an ideal gas. At 0°C and at a pressure of 1 atm it occupies a volume of 22.414 dm^3.

It means this law helps us to have a relationship between number of molecules of a gas and the volume occupied by it.

1.1.5 Dalton's law of partial pressures :

This law is for the mixture of gases. It was put forwarded by Dalton in 1801. According to this law, "the total pressure P of the mixture of gases which do not react with each other is equal to the sum of the partial pressures of constituent gases."

So,

$$P = p_1 + p_2 + p_3 + \ldots\ldots$$

∴ p_1, p_2 and p_3 are the partial pressures of the individual gases.

When all the gases are ideal, then they individually obey the general gas equation so,

$$P_1 = n_1 \frac{RT}{V}$$

$$P_2 = n_2 \frac{RT}{V}$$

$$P_3 = n_3 \frac{RT}{V}$$

The total pressure 'P' of the mixture of these three gases is sum of these partial pressures.

$$P = n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$

$$\therefore \quad n_1 + n_2 + n_3 = n$$

$$P = n \frac{RT}{V}$$

Where 'n' is the total number of moles of gases. The partial pressure of any gas is related with the mole fraction of the gas and the total pressure as follows.

$$P_1 = \frac{n_1}{n} P \qquad\qquad P_1 = x_1 P$$

$$P_2 = \frac{n_2}{n} P \qquad\qquad P_2 = x_2 P$$

$$P_3 = \frac{n_3}{n} P \qquad\qquad P_3 = x_3 P$$

Where x_1, x_2 and x_3 are mole fractions of the individual gases.

1.1.6 Graham's law of diffusion:

Graham in 1829, observed the spreading out or diffusion of gases. He postulated that the rate of the diffusion of the gas does not depend upon the gravity, but it depends upon temperature of gas. This law states that, "*rate of diffusion of a gas is inversely proportional to the square root of the density of the gas at a given temperature.*"

$$r \propto \frac{1}{\sqrt{d}}$$

If we have two gases having rates of diffusion as r_1, r_2, with densities d_1 and d_2, then

$$r_1 \propto \frac{1}{\sqrt{d_1}}$$

$$r_2 \propto \frac{1}{\sqrt{d_2}}$$

Dividing the two equations,

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

We also know that densities are directly proportional to the molar masses, so,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

It means that the rate of diffusion can be calculated from the densities of gases and molar masses of the gases.

1.1.7 Gay Lussac's law:

Joseph Gay Lussac in 1802, established the pressure temperature law which is called Gay Lussac's law. This law states that,

"The pressure of the fixed mass of the gas is directly proportional to Kelvin temperature at constant volume"

$$P \propto T \qquad \text{(when 'V' and 'n' are constant)}$$
$$P = kT$$
$$\frac{P}{T} = k$$

At more than one pressures and temperatures for the same quantity of the same gas,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Molar Volume:

It follows from Avogadro's law that one mole of any gas at a given temperature 'T' and pressure 'P' has the same fixed volume.

In order to compare the molar volume of gases, reference temperature and pressure have been fixed which is 0°C and one atm pressure.

It is found experimentally that one mole of any gas at S.T.P. occupies the volume of 22.414 dm³.

1.2.0 KINETIC MOLECULAR THEORY OF GASES

Introduction:

We have discussed the gas laws. which give us the general behaviour of gases. These laws are based on experimental observations and they are almost independent of the nature of gas.

If we want to discuss the behaviour of gases quantitatively, then we should appreciate the kinetic theory of gases given by Bernoulli in 1738. He was the first person who proposed that the pressure of the gas is due to the collisions of the gas molecules at the walls of the vessel. These proposals of Bernoulli led Clausius

(1857) to derive the kinetic equation. From his kinetic equation of gases, he was able to derive the gas laws. This theory was elaborated and extended by Maxwell, Boltzmann and Van der Waal.

Postulates of kinetic molecular theory:

(i) The gases are consisted of tiny particles called molecules. It means that gases like He, Ne, Ar etc are said to be monoatomic gases.

(ii) The molecules of a gas move randomly, collide among themselves, collide with the walls of the vessel and change their directions.

(iii) The pressure on the walls of the vessel is due to collisions on the walls.

(iv) The collisions of the molecules among themselves and on the walls of the vessel are perfectly elastic.

(v) The molecules of the gases are widely separated from each o er at ordinary temperature and pressure.

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

(vii) The actual volume of the gas molecules is negligible as compared to the volume of the vessel.

(viii) The force of gravity has almost no influence on the molecules of the gas.

(ix) The kinetic energy of the gas molecules is proportional to the absolute temperature of gas.

1.2.1 Mathematical derivation of kinetic equation of gases:

Let us consider a certain mass of gas in a cubic vessel of length 'l'. The total number of molecules in the vessel are 'n'. The mass of each molecule is 'm'. The individual component velocities along x, y, and z-axis are u, v and w respectively. These motions are shown in the Fig. (3).
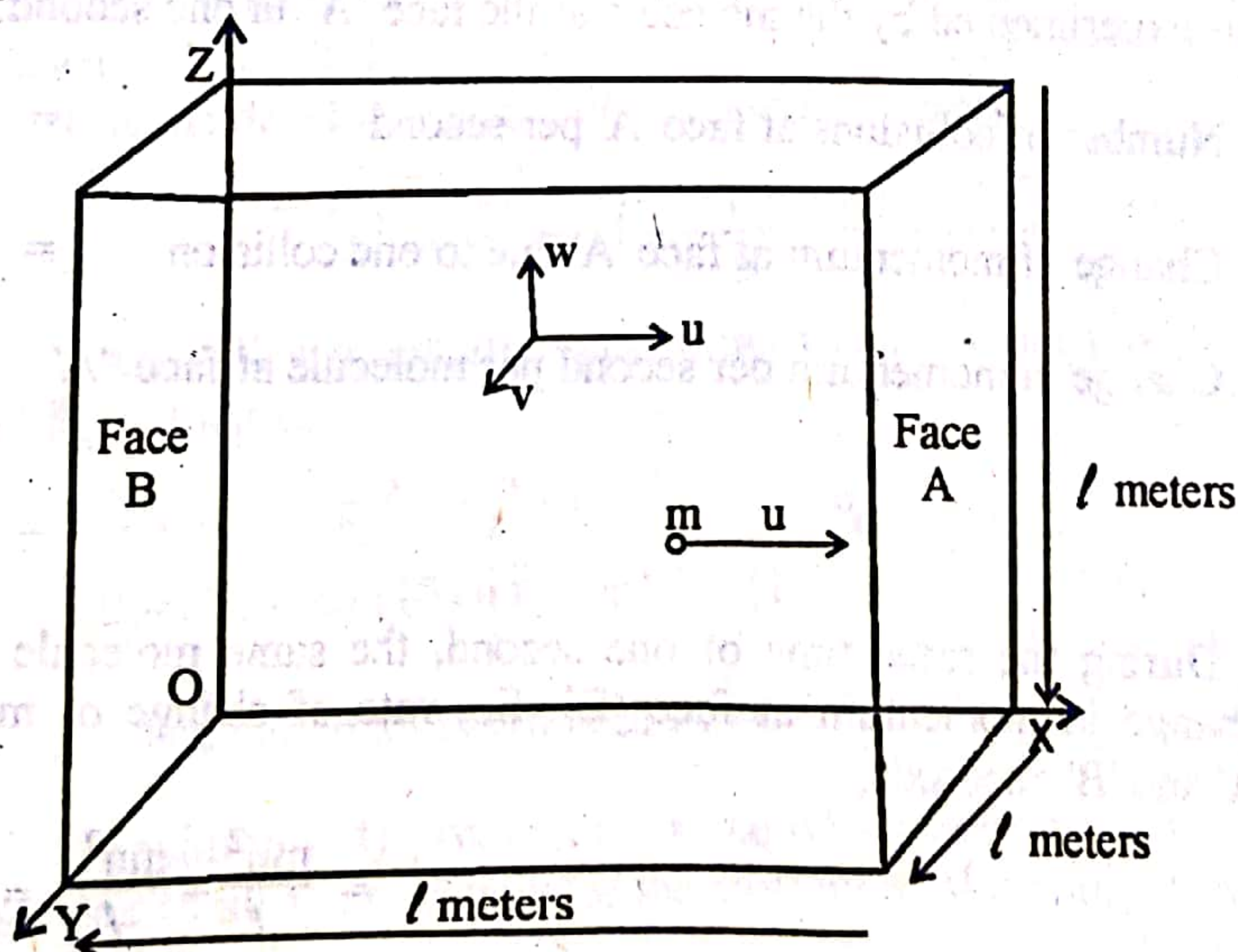

Fig. (3) Motion of molecules in three d'mensional space.

The actual velocity of a gas molecule is 'c'. The relationship of this velocity with component velocities is,

...... (1)

$$c^2 = u^2 + v^2 + w^2$$

Actually, we want to calculate the total effect of impact of all the molecules on the walls of the cube. For this purpose, we have to consider a single molecule.

Take into consideration a molecule of mass 'm' moving with velocity 'u' m. sec^{-1} along x-axis. It moves to the right side and collides with the face 'A' since the collision is elastic, it will rebound with velocity '−u'. During this collision the velocity remains unchanged, but the direction of motion changes.

Momentum of molecule before collision $= mu$

Momentum of molecule after collision $= -mu$

Change in momentum per molecule per single collision $= mu - (-mu)$

$= 2mu$ ...... (2)

If the molecule 'A' has to come back to its original position from where it started, then it should strike the face 'B' on x-axis. In this way, it has to cover a distance of '2l' meters.

'2l' meters covered distance makes collisions at face 'A' = 1

1 meter covered distance makes collisions at face $A = \dfrac{1}{2l}$

'u' meters covered distance makes collision at face $A = \dfrac{u}{2l}$

Since the velocity of molecule is 'u' ms^{-1}, so $\dfrac{u}{2l}$ is the number of collisions experimented by the molecule at the face 'A' in one second.

Number of collisions at face 'A' per second $= \dfrac{u}{2l}$ ... (3)

Change of momentum at face 'A' due to one collision $= 2\,mu$ ... (2)

Change in momentum per second per molecule at face 'A' $= 2mu \times \dfrac{u}{2l}$

$= \dfrac{mu^2}{l}$ ... (4)

During the same time of one second, the same molecule is suffering the same change in momentum at face 'B'. So, rate of change of momentum at the faces 'A' and 'B' on x-axis,

$$= \dfrac{mu^2}{l} + \dfrac{mu^2}{l} = \dfrac{2mu^2}{l} \quad ... (5)$$

Velocity of same molecule of mass 'm' is 'v' ms^{-1} on y-axis,

$$\therefore \text{ Rate of change of momentum along y-axis} = \frac{2mv^2}{\ell} \cdots (6)$$

Velocity of molecule on z-axis is 'w' ms^{-1}.

$$\therefore \text{ Rate of change of momentum along z-axis} = \frac{2mw^2}{\ell} \cdots (7)$$

Total rate of change of momentum, if the molecule is able to strick all the six faces is obtained from equation (5), (6) and (7), and that is

$$= \frac{2\,mu^2}{\ell} + \frac{2\,mv^2}{\ell} + \frac{2\,mw^2}{\ell} = \frac{2m}{\ell}(u^2 + v^2 + w^2) \quad \cdots (8)$$

Putting the value of $(u^2 + v^2 + w^2)$ from equation (1)

$$\text{Rate of change of momentum per molecule on six faces of cube} = \frac{2mc^2}{\ell} \quad \cdots (9)$$

According to Newton's laws of motion, the rate of change of momentum is equal to the force.

$$\therefore \text{ Force due to the collisions of a gas molecule on the six faces of the cube}$$

$$= \frac{2mc^2}{\ell} \text{ Newtons } \cdots (10)$$

Actually, we do not have a single molecule in the vessel. Suppose, we have 'n' molecules with velocities c_1, c_2, c_3 .... c_n.

The total force due to 'n' molecules on all the six faces of the cube

$$= \frac{2m}{\ell}(c_1^2 + c_2^2 + c_3^2 + \cdots\cdots\cdots c_n^2) \quad \cdots (11)$$

Equation (11) shows that in order to calculate the total force due to all the molecules, we have to consider millions and millions of the terms. The reasons is that every molecule has its own velocity and has its own momentum. In order to cover it, let us develop the idea of mean square velocity

$$\bar{c}^2 = \frac{c_1^2 + c_2^2 + c_3^2 + \cdots\cdots\cdots c_n^2}{n} \quad \cdots (12)$$

According to equation (12) mean square velocity is the mean of the square of all the velocities.

Hence, $c_1^2 + c_2^2 + c_3^2 + \cdots\cdots\cdots c_n^2 = n\bar{c}^2$ $\cdots (13)$

Put equation (13) into equation (11)

$$\text{Force due to all the molecules} = \frac{2mn\bar{c}^2}{\ell} \quad \cdots (14)$$

Equation (14) gives us the force which is being exerted on the walls of the vessel due to all the collisions of the molecules. We want to convert this force into pressure.

We know that the pressure is the force per unit area.

$$P = \frac{force}{area} \quad \cdots (15)$$

$$Force = \frac{2 \, mn\bar{c}^2}{\ell}$$

$$Area = 6\ell^2 (\text{area of each wall in } \ell^2) \quad \cdots (16)$$

Putting equations (14) and (16) in the equation of pressure (15).

$$P = \frac{2mn\bar{c}^2}{\ell \times 6\ell^2} = \frac{1}{3} \frac{mn\bar{c}^2}{V} \quad (\because \, V = \ell^3)$$

$$PV = \frac{1}{3} mn\bar{c}^2 \quad \cdots (17)$$

Equation (17) is the kinetic equation of the ideal gases. This equation tells us that the product 'PV' for any gas is equal to the $\frac{1}{3}$ of the mass of all the molecules i.e. 'mn', multiplied by mean square velocity of gas molecules ($\bar{c}^2$).

1.2.2 Derivation of gas laws from kinetic equation:

(i) Boyle's law:

In order to derive the Boyle's law, we take the help of postulates of kinetic theory relating the kinetic energy and absolute temperature. According to that postulate, kinetic energy is directly proportional to absolute temperature.

$$\frac{1}{2} mn\bar{c}^2 \propto T$$

$$\frac{1}{2} mn\bar{c}^2 = kT \quad \cdots (1)$$

$\therefore$ 'k' is proportionality constant

Kinetic equation of gas says that,

$$PV = \frac{1}{3} mn\bar{c}^2$$

or

$$PV = \frac{2}{3} \left(\frac{1}{2} mn\bar{c}^2 \right) \quad \cdots (2)$$

Putting equation (1) in (2)

$$PV = \frac{2}{3} (kT)$$

Let us put, $\frac{2}{3} k = k_1$ (another constant)

$$PV = k_1 T \quad \cdots (3)$$

If temperature is constant, then R.H.S. of equation (3) is constant.

So, $PV = $ constant

In this way, we have proved that at constant temperature the product of pressure and volume is a constant quantity.

(ii)   Charles's law:

In order to justify the Charles's law, we take the help of equation (3) from previous discussion

$$PV = k_1 T$$

$$\frac{V}{T} = \frac{k_1}{P} \qquad \cdots\cdots (4)$$

When the pressure is constant, the R.H.S. of this equation (4) is constant.

So, $$\frac{V}{T} = constant$$

This is the statement of Charles's law.

(iii)   Avogadro's law:

In this law, we have to prove that the equal volumes of all the ideal gases at same temperature and pressure contain equal number of molecules. Let us consider two gases with masses of molecules 'm_1' and 'm_2', having the root mean square velocities '$\bar{c}_1^2$', '$\bar{c}_2^2$'. Let the number of molecules be 'n_1' and 'n_2'. If these gases have the same pressure and volume, then

$$PV = \frac{1}{3} m_1 n_1 \bar{c}_1^2 \quad and \quad PV = \frac{1}{3} m_2 n_2 \bar{c}_2^2$$

So, $$\frac{1}{3} m_1 n_1 \bar{c}_1^2 = \frac{1}{3} m_2 n_2 \bar{c}_2^2$$

$$m_1 n_1 \bar{c}_1^2 = m_2 n_2 \bar{c}_2^2 \qquad \cdots\cdots (5)$$

If these two gases are maintained at same temperature, then their kinetic energies are same.

So, $$\frac{1}{2} m_1 \bar{c}_1^2 = \frac{1}{2} m_2 \bar{c}_2^2$$

$$m_1 \bar{c}_1^2 = m_2 \bar{c}_2^2 \qquad \cdots\cdots (6)$$

Dividing equation (5) by (6), we get

$$n_1 = n_2$$

So, we have proved that when two gases are maintained at same P, V, and T, then their number of molecules 'n', are same.

(iv)   Graham's law of diffusion:

This law states that the rate of diffusion of a gas is inversely proportional to the square root of the density of the gas.

For this purpose, let us consider that we have one mole of an ideal gas,

So, $$n = N_A$$

Hence, kinetic equation becomes,

$$PV = \frac{1}{3}mN_A\bar{c}^2 \qquad \cdots\cdots (7)$$

This equation (7) is the kinetic equation for one mole of a gas.

$$m \times N_A = M \text{ (Molar mass of the gas)}$$

So, $$PV = \frac{1}{3}M\bar{c}^2 \qquad \cdots\cdots (8)$$

Equation (8) is also kinetic equation for one mole ideal gases. Rearranging the above equation (8),

$$\bar{c}^2 = \frac{3PV}{M} = \frac{3P}{M/V} \qquad \text{since, } \left(d = \frac{M}{V}\right)$$

$$\bar{c}^2 = \frac{3P}{d} \qquad \cdots\cdots (9)$$

Taking the square root of equation (9) on both sides

$$\sqrt{\bar{c}^2} = \sqrt{\frac{3P}{d}}$$

$\sqrt{\bar{c}^2}$, is the square root of mean square velocity and it is simply the rate of diffusion (r) of gas.

So, $$r = \sqrt{\frac{3P}{d}}$$

If pressure is constant, then

$$r \propto \frac{1}{\sqrt{d}} \qquad \cdots\cdots (10)$$

This is the Graham's law of diffusion.

1.2.3 Molecular velocities:

It is a known fact that the molecules of a gas move haphazardly, collide among themselves and with the walls of the vessel. So the molecules have certain velocities. All the molecules of a gas do not have the same velocities at a given temperature. For this reason, various types of velocities have been designed which are as follows

    (a)   Root mean square velocity

    (b)   Average velocity

    (c)   Most probable velocity.

(a)   **Root mean square velocity:**

The mathematical expression for root mean square velocity can be derived from kinetic equation of gases, i.e.,

$$PV = \frac{1}{3}mn\bar{c}^2$$

Suppose, that gas is one mole, so

$$n = N_A$$

$$PV = \frac{1}{3} m N_A \bar{c}^2 \qquad \cdots\cdots (1)$$

Equation (1) is the kinetic equation of gases for one mole of the gas. General gas equation for one mole is

$$PV = RT \qquad \cdots\cdots (2)$$

Comparing equation (1) and (2)

$$\frac{1}{3} m N_A \bar{c}^2 = RT \qquad \because mN_A = M$$

$$\frac{1}{3} M\bar{c}^2 = RT$$

or $$\bar{c}^2 = \frac{3RT}{M} \qquad \cdots\cdots (3)$$

According to equation (3) the mean square velocity of gas molecules depends upon the ==temperature and the molar mass.== If we take the square root of the equation (3), then ==we get the root mean square velocity.==

$$\sqrt{\bar{c}^2} = \sqrt{\frac{3RT}{M}}$$

$$c_{r.m.s} = \sqrt{\frac{3RT}{M}} = \sqrt{3} \sqrt{\frac{RT}{M}} = 1.732 \sqrt{\frac{RT}{M}}$$

$$c_{rm.s} = 1.732 \sqrt{\frac{RT}{M}} \qquad \cdots\cdots (4)$$

According to equation (4), the root mean square velocity $c_{r.m.s}$ of the gas molecules is directly proportional to the square root of absolute temperature and inversely proportional to the square root of molar mass.

It means heavier molecules with greater molar mass move slowly. Moreover, we come to know that the elevated temperature makes the molecules to move faster.

(b) Average velocity:

This is also called mean velocity and it is *"the mean of the all the possible velocities."* It is denoted by $\bar{c}$.

$$\bar{c} = \frac{c_1 + c_2 + c_3 + \cdots\cdots c_n}{n}$$

The expression for $\bar{c}$ can be obtained from Maxwell's law of distribution of velocities.

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8}{\pi}} \sqrt{\frac{RT}{M}} = 1.59 \sqrt{\frac{RT}{M}}$$

$$\bar{c} = 1.59 \sqrt{\frac{RT}{M}} \qquad \cdots\cdots (5)$$

Average velocity also depends upon the temperature and the molar mass of the gas just like root mean square velocity given by equation (4).

(c) Most probable velocity:

It is defined as, "*the velocity possessed by greatest fraction of the molecules in a gas at any temperature.*"

Actually, all the molecules of the gas have not equal velocities. Molecules are distributed in groups of velocities. These groups may be called as fractions. All these fractions are not equal. That fraction which is biggest possesses a certain velocity and is called most probable velocity. It is obtained by plotting a graph between velocities of molecules on x-axis and fractions of molecules on y-axis. Its expression is as follows.

$$c_{m.p} = \sqrt{\frac{2RT}{M}} = \sqrt{2}\sqrt{\frac{RT}{M}} = 1.414\sqrt{\frac{RT}{M}}$$

$$c_{m.p} = 1.414\sqrt{\frac{RT}{M}} \qquad \cdots\cdots (6)$$

Equation (6) also tells us that most probable velocity is directly proportional to the square root of absolute temperature and inversely proportional to the square root of molar mass of the gas.

Comparison of velocities:

By using above formula for three types of velocities, we can calculate their values by putting the values of temperature and molar mass. Anyhow, the ratio of the velocities will remain the same, if the molar mass is same and they are maintained at same temperature.

$$c_{r.m.s} \quad : \quad \bar{c} \quad : \quad c_{m.p}$$

$$1.732\sqrt{\frac{RT}{M}} \quad : \quad 1.59\sqrt{\frac{RT}{M}} \quad : \quad 1.414\sqrt{\frac{RT}{M}}$$

$$1.732 \quad : \quad 1.59 \quad : \quad 1.414$$

It means that root mean square velocity of a gas is of maximum value and most probable is the least value among the three velocities.

EXAMPLE (1)

Calculate the $C_{r.m.s}$, $\bar{C}$ and C_{mp} of O_2 molecule at 25°C. What do you expect these velocities for H_2 will be at 25°C.

SOLUTION:

The molar mass of 'O_2' molecule should be taken in kg, because the value of "R" is in J K^{-1} mol^{-1}.

$$M = 32 \times 10^{-3} = 0.032 \text{ kg mol}^{-1}$$
$$T = 25\,°C + 273 = 298°\,K$$
$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

[handwritten margin notes] group of molecules & fractions

Putting the values in equation for various velocities

$$C_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298° \text{ K}}{0.032 \text{ kg mol}^{-1}}}$$

$$= \sqrt{\frac{7432.716 \text{ m}^2\text{s}^{-2}}{0.032}} = \boxed{481.9 \text{ ms}^{-1}} \quad \text{Ans.}$$

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

$$\bar{c} = \sqrt{\frac{8 \times 8.3143 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{3.143 \times 0.032 \text{ kg mol}^{-1}}}$$

$$\bar{c} = \sqrt{\frac{19821.3 \text{ m}^2 \text{ s}^{-2}}{0.10048}} = \boxed{441.13 \text{ ms}^{-1}} \quad \text{Ans.}$$

$$C_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{0.032 \text{ kg mol}^{-1}}}$$

$$C_{mp} = \sqrt{\frac{4955.144 \text{ m}^2\text{s}^{-2}}{0.032}} = \boxed{393.5 \text{ ms}^{-1}} \quad \text{Ans.}$$

Because the molar mass of H_2 is 16 times less than that of O_2, so the above calculated velocities for H_2 will be four times higher than that of O_2 at 25°C.

EXAMPLE (2)

At what temperature will the C_{rms} of SO_2 be the same as that of O_2 at 27°C.

SOLUTION:

Let us suppose that the temperature is 'T_1' at which SO_2 would have the same root mean square velocity as O_2 at 27°C.

Since we donot have to put the value of R in any given units in the numerical, so, the unit of molar mass may be in g mol^{-1}

$$C_{rms} (SO_2) = \sqrt{\frac{3RT_1}{64}}$$

For O_2 the C_{rms} velocity at 27°C (300 K) is

$$C_{rms} (O_2) = \sqrt{\frac{3R \times 300}{32}}$$

Since velocities of both are same, so

So, $$\sqrt{\frac{3RT_1}{64}} = \sqrt{\frac{3R \times 300}{32}}$$

Squaring both sides, we get

$$\frac{3RT_1}{64} = \frac{3R \times 300}{32}$$

$$T_1 = \frac{300 \times 64}{32} = 600 \text{ K}$$

or $$T_1 = 600 - 273 = \boxed{327°C} \quad \text{Ans.}$$

1.2.4 Kinetic energy of one mole of a monoatomic ideal gas:

The kinetic equation of gases can help us to derive the formula for kinetic energy possessed by one mole of an ideal gas irrespective of the nature of the gas. The basic condition is that the gas should be monoatomic. We know that

$$PV = \frac{1}{3}mn\bar{c}^2$$

If the gas is one mole, then

$$n = N_A$$

$$PV = \frac{1}{3}mN_A\bar{c}^2 \qquad mN_A = M \text{(molar mass)}$$

$$PV = \frac{1}{3}M\bar{c}^2 \qquad \qquad \cdots\cdots (1)$$

The general gas equation for one mole of gas is

$$PV = RT \qquad \qquad \cdots\cdots (2)$$

Comparing the equation (1) and equation (2)

$$\frac{1}{3}M\bar{c}^2 = RT \qquad \qquad \cdots\cdots (3)$$

Multiply and divide L.H.S. of equation (3) with '2'

$$\frac{2}{3}\left(\frac{1}{2}M\bar{c}^2\right) = RT$$

$$\frac{1}{2}M\bar{c}^2 = \frac{3}{2}RT$$

$$E_k = \frac{3}{2}RT \qquad \qquad \cdots\cdots (4)$$

According to equation (4), the kinetic energy of one mole of an ideal gas depends upon the temperature of the gas and not upon its nature.

Remember that, if the gas is diatomic or polyatomic, then some extra energy is required to maintain the rotational and vibrational motions of the monoatomic gas.

EXAMPLE (3)

Calculate translational kinetic energy for 2 moles of a gas at 27°C.

SOLUTION:

For 1 mole of a gas, K.E. $= \frac{3}{2}RT$

So, for 2 moles of the gas,

$$\text{K.E.} = \left(\frac{3}{2}RT\right) \times 2$$

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

and $T = 27°C = (27 + 273) \text{ K} = 300 \text{ K}$

$$\text{Kinetic energy} = \frac{3}{2} \times 8.3143 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times 2 \text{ moles}$$

$$= \boxed{7482.6 \text{ Joules}} \qquad \text{Ans.}$$

1.2.5 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. ϵ_k.

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

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

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

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

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

1.3.0 HEAT CAPACITIES OF GASES

Matter exists due to the possession of energy and there is a close interaction between energy and matter. Matter has a capability to retain to a greater or lesser extent certain amount of energies. In this article, we have to look at the capabilities of the gases to absorb various amounts of energies by the change of temperature.

Heat capacity of a gas is the amount of heat required to raise the temperature of the gas by 1°C (1 K). If the quantity of the substance is 1 mole, then the amount of heat required to raise the temperature is molar heat capacity.

If the weight of the gas is one gram, then it is called specific heat.

Heat capacities are denoted by C. The rise of temperature is noted from 14.5°C to 15.5°C. It is measured in calories K^{-1} mol^{-1} in non SI units. In SI units the molar heat capacity is expressed as JK^{-1} mol^{-1}.

1.3.1 Types of heat capacities:

Heat capacities are of two types

(i) Heat capacity at constant volume (C_v)

(ii) Heat capacity at constant pressure (C_p)

(i) **Heat capacity at constant volume (C_v):**

"It is the amount of heat which is required to raise the temperature of one mole of a gas by 1°C, when the volume is kept constant and the pressure is allowed to increase."

We are going to discuss only monoatomic gases at the moment. Monoatomic gases have only translational motion and the kinetic energy possessed by one mole of monoatomic gas is given by

$$E_K = \frac{3}{2}RT \qquad \qquad \text{......} (1)$$

Let us increase the temperature of this monoatomic ideal gas by 1°C. Temperature change is from T to (T+1), and its kinetic energy K'_k at (T+1) C°, is

$$E'_k = \frac{3}{2} R(T + 1) \qquad \ldots\ldots (2)$$

Substracting equation (1) from equation (2)

$$E'_k - E_k = C_V = \frac{3}{2} R(T + 1) - \frac{3}{2} RT$$

$$C_V = \frac{3}{2} R \qquad \ldots\ldots (3)$$

Since, $R = 8.3193 \text{ JK}^{-1} \text{ mol}^{-1}$

So, $\qquad C_V = \frac{3}{2} (8.3143 \text{ J K}^{-1} \text{ mol}^{-1}) = 12.48 \text{ J K}^{-1} \text{ mol}^{-1}$

It means that if we have one mole of a monoatomic gas, then molecules will absorb same amount of heat i.e., $\frac{3}{2}$R, when their temperatures are increased by one Kelvin.

Reason:

It has been observed that, the monoatomic gas like He, Ne, Ar and vapours of Hg, K and other metals have C_V value of 12.48 J K^{-1} mol^{-1}. The reason is that, the one mole of all the monoatomic elements have Avogadro's number of atoms. In other words 12.48 Joules is the demand of Avogadro's number of atoms, when we change their temperature by 1°C (1 °K) say for He, Ne, Ar etc.

(ii)   Heat capacity at constant pressure (C_p):

"*It is the amount of heat required to raise the temperature of one mole of a gas by 1°C (1 K) keeping the pressure constant and the volume is allowed to increase.*" It is denoted by C_p.

Actually, when we measure C_p value of a gas then some energy is expended in expansion of the gas and pressure volume work is done. Let us calculate the additional pressure volume work.

The general gas equation for one mole of an ideal gas is

$$PV = RT \qquad \ldots\ldots (4)$$

Suppose that by increasing the temperature by one Kelvin from T to (T + 1), the volume changes from V to (V + ΔV), so

$$P(V + \Delta V) = R(T + 1) \qquad \ldots\ldots (5)$$

or $\qquad PV + P\Delta V = RT + R \qquad \ldots\ldots (6)$

Substituting equation (4) in equation (6),

$$RT + P\Delta V = RT + R$$

So, $\qquad P\Delta V = R \qquad \ldots\ldots (7)$

It means that 'R' is the contribution to the molar heat capacity due to the external work. It means that the value of the C_p should be as follows

$$C_P = \frac{3}{2}R + R = \frac{5}{2}R \qquad \ldots\ldots (8)$$

Substituting the value of the general gas constant 'R', as 8.3143 JK^{-1} mol^{-1}.

$$C_P = \frac{5}{2}(8.3143 \ J \ K^{-1} \ mol^{-1}) = 20.8 \ J \ K^{-1} \ mol^{-1}$$

It means that for monoatomic ideal gases, the amount of heat required to raise the temperature by one Kelvin for one mole along with the increase of volume is 20.8 J.

1.3.2 Important conclusions for C_p and C_v:

From the expressions of C_p and C_v, two important conclusions can be drawn.

(i) $\qquad C_P - C_V = \frac{5}{2}R - \frac{3}{2}R = R$

Whatever is the atomicity of the gas, the difference remains the same.

(ii) $\quad$ For monoatomic gases, the ratio of two heat capacities (γ) is same i.e., 1.666.

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.666$$

1.3.3 Polyatomic gases:

The gases which contain two or more atoms in their molecules have higher values of C_p and C_v from those of monoatomic gases. The reason is that, monoatomic gases only need translational energies while polyatomic gases spend their energies for rotational and vibrational motions as well. So for polyatomic gases,

$$C_V = \frac{3}{2}R + X$$

$$C_P = \frac{5}{2}R + X$$

'X' is the contribution of energy for rotational and vibrational motions. Two important conclusions are,

(i) $\quad C_P - C_V = \left(\frac{5}{2}R + X\right) - \left(\frac{3}{2}R + X\right) = R$

(ii) $\quad \dfrac{C_P}{C_V} = \gamma = \dfrac{\frac{5}{2}R + X}{\frac{3}{2}R + X} < 1.666$

The table (1) gives us the C_p, C_v and γ-values for various gases

Table (1) Heat capacity of gases at 25°C (J K^{-1} mol^{-1})

Gases	C_p	C_v	$C_p - C_v$	γ
Argon	20.84	12.49	8.31	1.66
Helium	20.79	12.48	8.31	1.66
Mercury vapour	20.66	12.38	8.28	1.66
Iodine vapour	20.80	12.48	8.32	1.67
Chlorine	33.84	25.03	8.81	1.35
Hydrogen	28.80	20.52	8.28	1.41
Hydrogen chloride	29.12	20.82	8.30	1.41
Nitrogen	29.10	20.81	8.29	1.40
Oxygen	29.40	21.05	8.35	1.40
Carbon dioxide	37.10	28.81	8.29	1.30
Hydrogen sulphide	33.10	24.75	8.35	1.33
Nitrous oxide	32.58	25.26	8.32	1.32
Sulphur dioxide	38.10	29.32	8.88	1.30

1.4.0 LAW OF EQUIPARTITION OF ENERGY

Introduction:

For a monoatomic gas the translational energy associated with one mole of the molecules at any temperature is $\frac{3}{2}$ RT. "According to the law of equipartition of energy, $\frac{1}{2}$ RT is expended along x-axis, $\frac{1}{2}$ RT along y-axis and $\frac{1}{2}$ RT along z-axis."

$$E_K = \left(\frac{1}{2}RT\right)_x + \left(\frac{1}{2}RT\right)_y + \left(\frac{1}{2}RT\right)_z \qquad \ldots\ldots (1)$$

We have already considered that if the component velocities are u, v and w, then the kinetic energies along x, y and z-axis are,

$$E_K' = \frac{1}{2}M\bar{u}^2 + \frac{1}{2}M\bar{v}^2 + \frac{1}{2}M\bar{w}^2 \qquad \ldots\ldots (2)$$

$\bar{u}, \bar{v}$ and $\bar{w}$ are the average velocities along x, y, and z-axis.

If we want to apply this law on the equipartition of energy for the a single molecule, then equation (1) and (2) can be written as, (3) and (4) respectively.

$$\epsilon_K = \left(\frac{1}{2}kT\right)_x + \left(\frac{1}{2}kT\right)_y + \left(\frac{1}{2}kT\right)_z \qquad \ldots\ldots (3)$$

where 'k' is Boltzmann constant.

$$\text{or} \qquad \epsilon_K = \frac{1}{2}m\bar{u}^2 + \frac{1}{2}m\bar{v}^2 + \frac{1}{2}m\bar{w}^2 \qquad \ldots\ldots (4)$$

1.4.1 Degrees of freedom and atomicity of a gas:

In order to consider the distribution of energies for different modes of motion one should have the idea of the degree of freedom. *"Degree of freedom is the number of independent co-ordinates required to locate all the atoms in a molecule."* The location of an atom can be specified by three co-ordinates.

The total degrees of freedom of a molecule = 3N.

Where 'N' is the number of atoms in that molecule. Translational degrees of freedom are always three. Rotational degrees of freedom depend upon the fact that whether the molecule is linear or non-linear.

For a linear molecule, rotational degrees of freedom = 2

For a non-linear molecule, rotational degrees of freedom = 3

After the completion of rotational and translational degrees of freedom, we should calculate the vibrational degrees of freedom.

1.4.2 Degrees of freedom of a monoatomic molecule:

Total degrees of freedom $= 3 \times 1 = 3$

Translational degrees of freedom $= 3$

Rotational degrees of freedom $= 0$

Vibrational degrees of freedom $= 0$

So, the atoms of He, Ne, Ar, Kr, Hg and Na vapours spend their energies only for translational motions along x, y and z-axis, but not for rotational and vibrational motions

$$E_k = \left(\frac{1}{2}RT\right)_x + \left(\frac{1}{2}RT\right)_y + \left(\frac{1}{2}RT\right)_z = \frac{3}{2}RT$$

1.4.3 Degrees of freedom of a diatomic molecule:

Total degrees of freedom $= 3 \times 2 = 6$

Translational degrees of freedom $= 3$

Rotational degrees of freedom $= 2$ (diatomic molecule are always linear)

Vibrational degrees of freedom $= 6 - 3 - 2 = 1$

Energy expended for one translational degree of freedom $= \frac{1}{2}RT$

Energy expended for one rotational degree of freedom $= \frac{1}{2}RT$

Energy expended for one vibrational degree of freedom $= \frac{1}{2}RT + \frac{1}{2}RT$

$$= RT$$

$\left(\frac{1}{2}RT \text{ is kinetic energy and } \frac{1}{2}RT \text{ is potential energy}\right)$.

Now, let us do the calculations for total energy being expended by the diatomic linear molecule.

$$E_K = 3 \times \frac{1}{2}RT + 2 \times \frac{1}{2}RT + RT = \frac{3}{2}RT + RT + RT = 3.5\,RT$$

It means that a diatomic molecule like H_2, F_2 Cl_2, O_2, N_2, HCl etc. need the energy of 3.5 RT to maintain all their motions for six degrees of freedom. This energy is more than double than those of monoatomic molecules.

1.4.4 Degrees of freedom of triatomic molecules:

Triatomic linear:

Total degrees of freedom	$= 3 \times 3 = 9$
Translational degrees of freedom	$= 3$
Rotational degrees of freedom (linear)	$= 2$
Vibrational degrees of freedom (for linear)	$= 9 - 3 - 2 = 4$

Triatomic linear molecule likes CO_2, CS_2, COS, etc. have four vibrational degrees of freedom. The total energy can be calculated as follows.

$$E_K = 3 \times \frac{1}{2} RT + 2 \times \frac{1}{2} RT + 4 \times RT = 6.5 \, RT$$

Triatomic non-linear:

For triatomic non-linear molecules like H_2O, H_2S, H_2Se, SO_2, etc. the translational degrees of freedom are three, rotational are three and vibrational are also three. So total energy of such a molecule is,

$$E_K = 3 \times \frac{1}{2} RT + 3 \times \frac{1}{2} RT + 3RT = 6RT$$

It means that the total energy being expended by water is little bit less than that of CO_2.

1.4.5 Degrees of freedom of a tetra-atomic molecule:

Total degrees of freedom	$= 3 \times 4 = 12$
Translational degrees of freedom	$= 3$
Rotational degrees of freedom	$= 3$
Vibrational degrees of freedom	$= 12 - 3 - 3 = 6$

$$E_K = 3 \times \frac{1}{2} RT + 3 \times \frac{1}{2} RT + 6RT = 12RT$$

It means that energy possession goes an increasing for molecules having higher atomicities.

1.5.0 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. (4) (a)
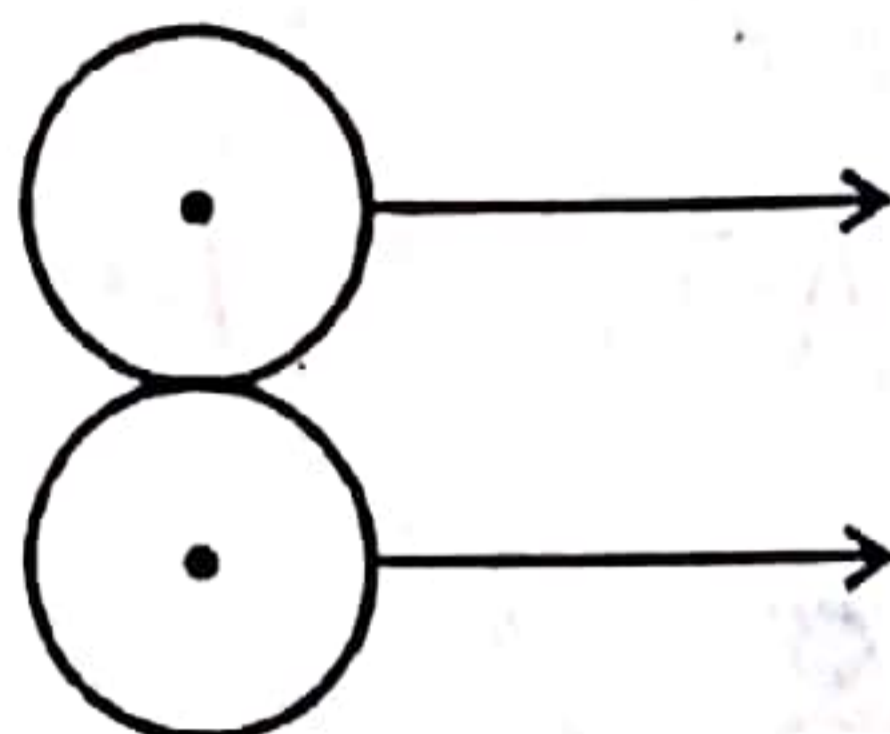
Fig. (4) (a) Grazing collision (relative velocity $\bar{c}$).

(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 4(b) shows the head on collision.
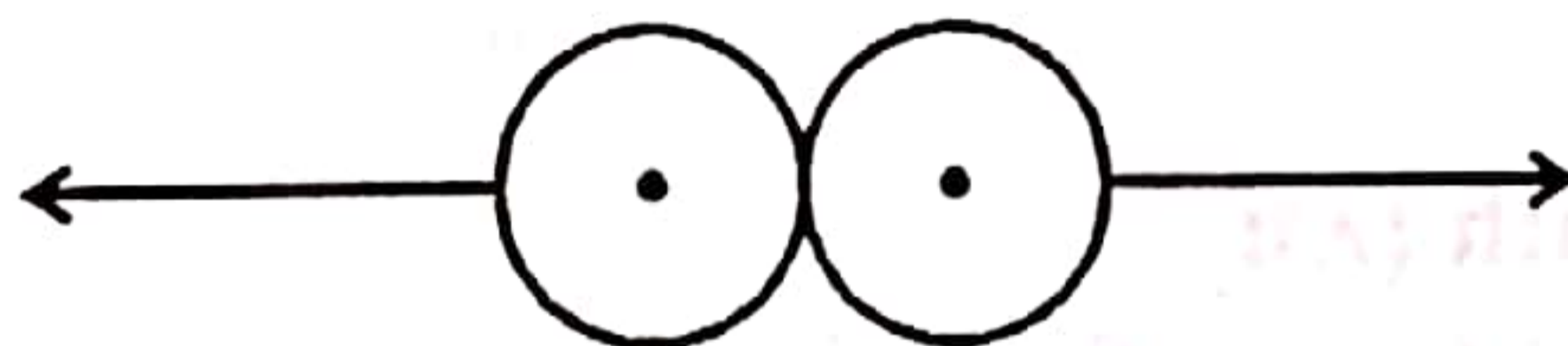
Reverse direction ?

Fig. (4) (b) Head on collision (relative velocity $2\bar{c}$).

(iii)   **Right angled collision:**

When two molecules approach each other and their approaching lines are approximately 90° to each other. Then the collision is right angled. The relative speed is '$\sqrt{2}\bar{c}$'. Following diagram 4(c) shows this collision
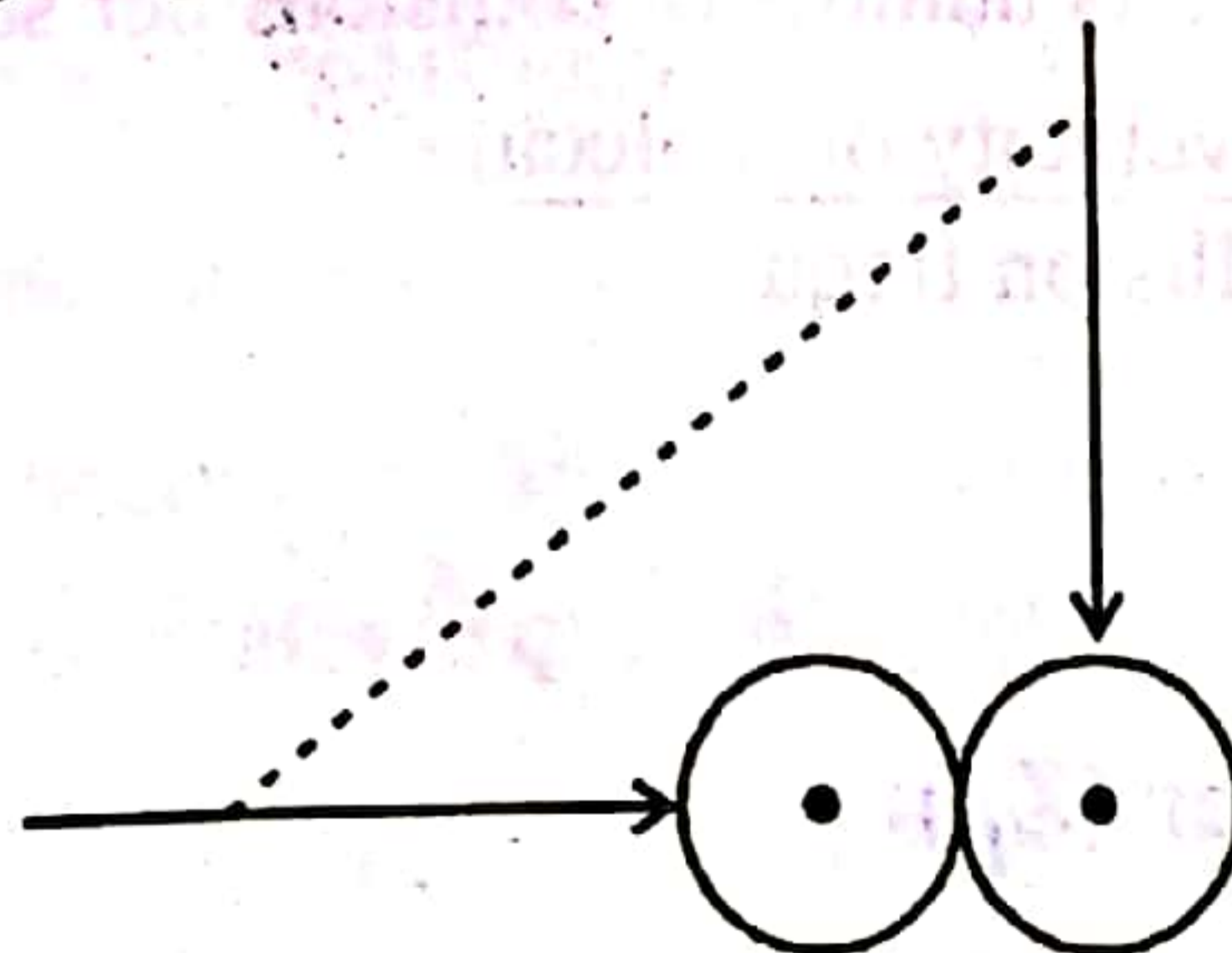
Fig. (4) (c) Right-angled collision (relative velocity $\sqrt{2}\bar{c}$)

Elastic collision:

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

1.5.1 Collision diameter:

In order to do the collision, the molecules approach each other. At the time of contact of 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. (5).

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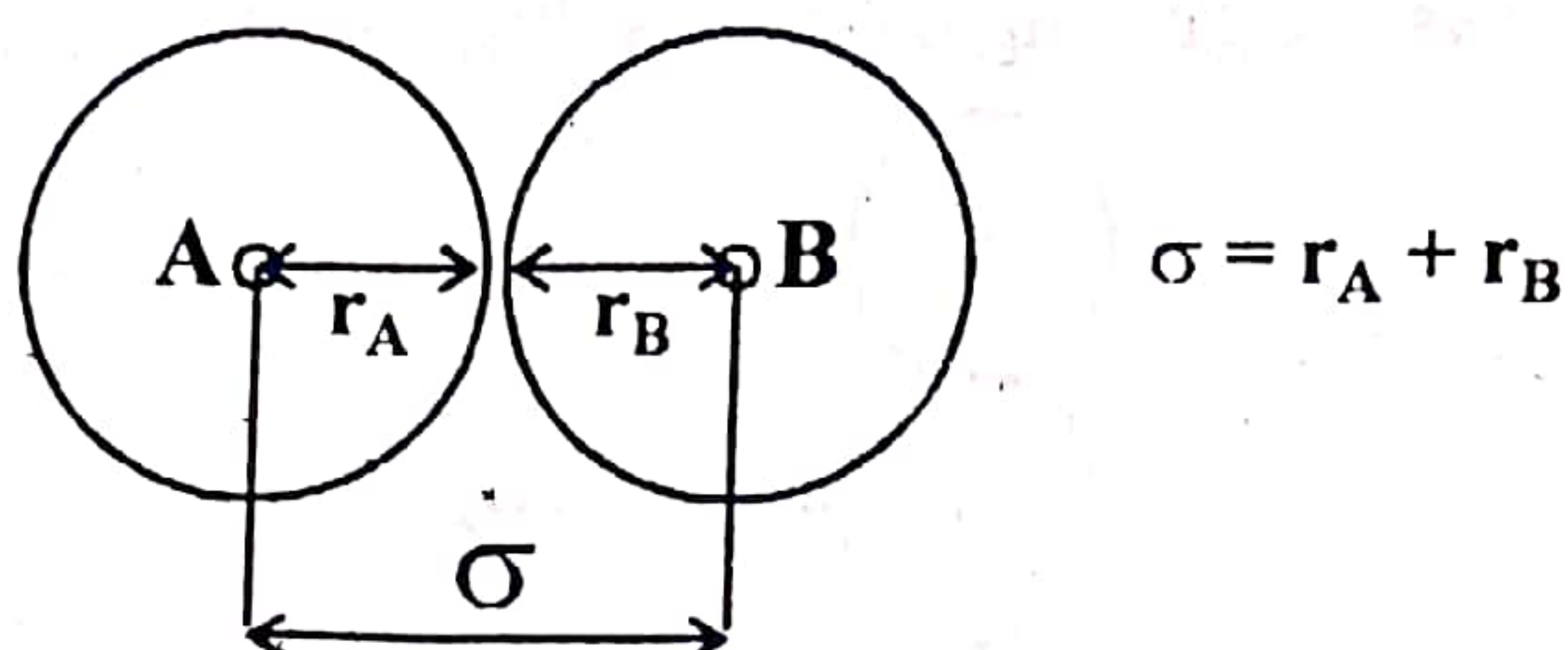

$$\sigma = r_A + r_B$$

Fig. (5) Collision diameter of two colliding molecules

1.5.2 Collision frequency (Z_I):

"If we follow a single molecule in one cm^3 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_I. Its value should depend upon the velocity of gas molecules, sizes of molecules and closeness of the molecules in the vessel.

1.5.3 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.

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

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

1.5.4 Collision number (Z_{II}):

"It is the number of collisions happening in all the molecules in 1 cm^3 of the gas in one second." It is denoted by 'Z_{II}'. Mathematically, we can say that,

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

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

1.5.5 Derivation for the expression of collision frequency (Z_1):

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 (6) makes the idea clear.
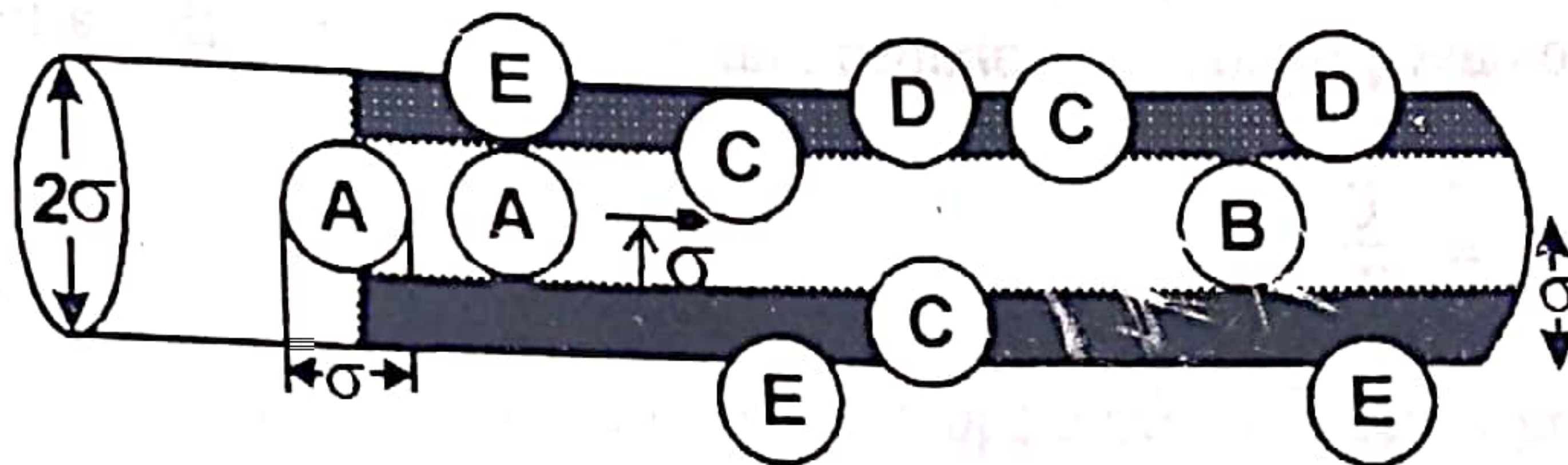

Fig. (6) Imaginary cylinder has many molecules and
one molecule (A) is travelling in the centre of the cylinder.

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 second should be $= \pi\sigma^2\bar{c} \, n$.

Be careful, that the number of right-angled collision is much greater than grazing 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 approaching each other to do right-angled collision, is '$\sqrt{2}\bar{c}$', and not '$\bar{c}$'. It means that considering the right-angled collisions, the length of the imaginary cylinder is proposed to be ' $\sqrt{2}\bar{c}$ '.

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

This is the collision frequency of the molecule.

1.5.6 Formula of mean free path (λ):

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

$$\lambda = \frac{\bar{c}}{Z_I} \qquad\qquad ...... (4)$$

Putting value of Z_1 from equation (3) into equation (4)

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

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2\,n} \; cm \; collision^{-1} \qquad ...... (5)$$

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

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

"Collision number is the number of collisions happening in all the molecules in one second in 1 cm³ 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 cm³.

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

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.

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

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

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:

$$\text{Molar mass of } O_2 = 32 \times 10^{-3} \text{ kg mol}^{-1}$$
$$\text{Temperature} = 25 \, C° + 273 = 298 \text{ K}$$
$$R = 8.3143 \text{ JK}^{-1} \text{ mol}^{-1}$$
$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

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

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

$$= 2.46 \times 10^{25} \text{ m}^{-3} \qquad = 2.46 \times 10^{22} \text{ dm}^{-3}$$

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

The collision frequency is the number of collisions per second.

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

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

$Z_1 = 1.414 \times 3.14 \times (3.60 \times 10^{-10}\ m^2)$

$\times (4.44 \times 10^2\ ms^{-1}) \times (2.64 \times 10^{25}\ m^{-3})$

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

The collision number is the number of collision per second per m^3

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

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

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

1.6.0 KINETIC THEORY OF GAS VISCOSITY

Introduction:

All forms of matter which have moving capabilities can show the viscosity. Gases and liquids fall in this category.

Viscosity of gas finds its explanation in kinetic molecular theory of gases. It is proposed that the gases travel in the form of layers just like liquids. Frictional force is created between the layers. The creation of the frictional force between the layers of liquids and gases are different from each other.

1.6.1 Gas viscosities:

In order to understand the viscosity of gases, suppose that a gas is flowing in a pipe from lower to the upper side as shown in the following diagram (7). Gas is travelling in the form of layers.
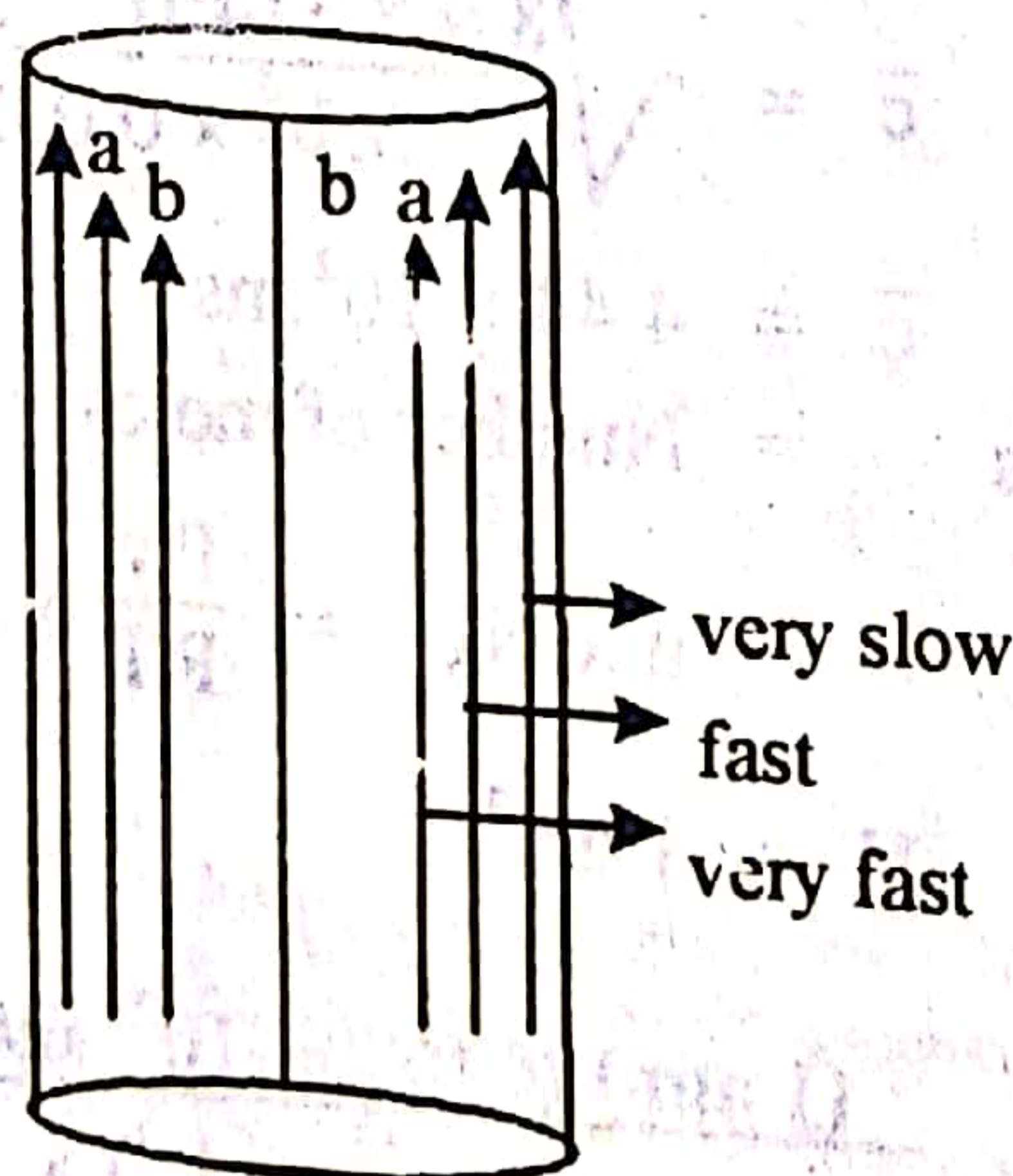

Fig. (7). Motion of gas molecules in a cylinder in the form of layers

We have considered two layers 'a' and 'b' in the diagram. 'a' is the outer layer and 'b' is the inner layer. The molecules in the layer 'a' are slower than the molecules of layer 'b'. The reason is that the 'a' layer is closer to the walls of the tube. There is a frictional force between the two layers.

How this frictional force is developed? Actually the molecules of layer 'a' migrate to layer 'b' and that of 'b' migrate to 'a'. It means that there is a transport of momentum from one layer to the other.

The molecules of the layer 'a' are moving slowly and they have less momentum. When they enter the molecules of the layer 'b', they decrease the momentum of the layer 'b'. So, the layer 'b' feels the retarding force.

"This retarding influence of the slower layer of gas on a fast moving one as a result of transport of momentum is called viscosity of a gas." In other words, we can say that viscosity of gas is the quantitative measurement of resistance of the flow of the layers of a gas.

1.6.2 Derivation for the formula of viscosity of gases:

When we shift from one layer of gas to the other, then there happens a change in the velocity of the layer. The layers towards the centre of the tube are faster and outer layers are slower.

"The rate of change of velocities of the layers with respect to perpendicular distance between them is called velocity gradient." Greater the velocity gradient, $\left(\dfrac{du}{dx}\right)$, greater the frictional force. Mathematically, we can say that,

$$f \propto - A\frac{du}{dx}$$

$$f = -A\eta\frac{du}{dx} \qquad \cdots\cdots (1)$$

In this equation 'f' is the frictional force between the layers ' $\dfrac{du}{dx}$ ' is the velocity gradient, 'η' is the co-efficient of viscosity and 'A' is the area of contact of two layers.

Co-efficient of viscosity (η):

"It is the force in Newtons which must be exerted between two parallel layers one square meter in area and one meter apart in order to maintain a streaming velocity of one meter per second of one layer past the other."

Units of η:

This can be explained from equation (1).

As, $\quad f = A\eta\frac{du}{dx}$

$$\boxed{1\ \text{Poise} = 10^{-1}\ \text{kg m}^{-1}\ \text{s}^{-1}}$$

So, $\quad \eta = \dfrac{f}{A\dfrac{du}{dx}}$

or $\quad \eta = \dfrac{f\,dx}{A\,du} = \dfrac{Nm}{m^2\,m\,s^{-1}} = Nm^{-2}\,s^{-1}$

$$= (\text{kg m s}^{-2})\,m^{-2}\,s^{+1} = \text{kg m}^{-1}\,s^{-1}$$

1.6.3 Relationship between viscosity and mean free path:

In order to derive the mathematical relationship, let us consider a gas consisting of several layers. These layers are separated by distance 'λ' which is the mean free path of the gas. These layers are moving parallel to the Y-axis as shown in the following diagram (8). The line 'oy' shows the wall of the tube.
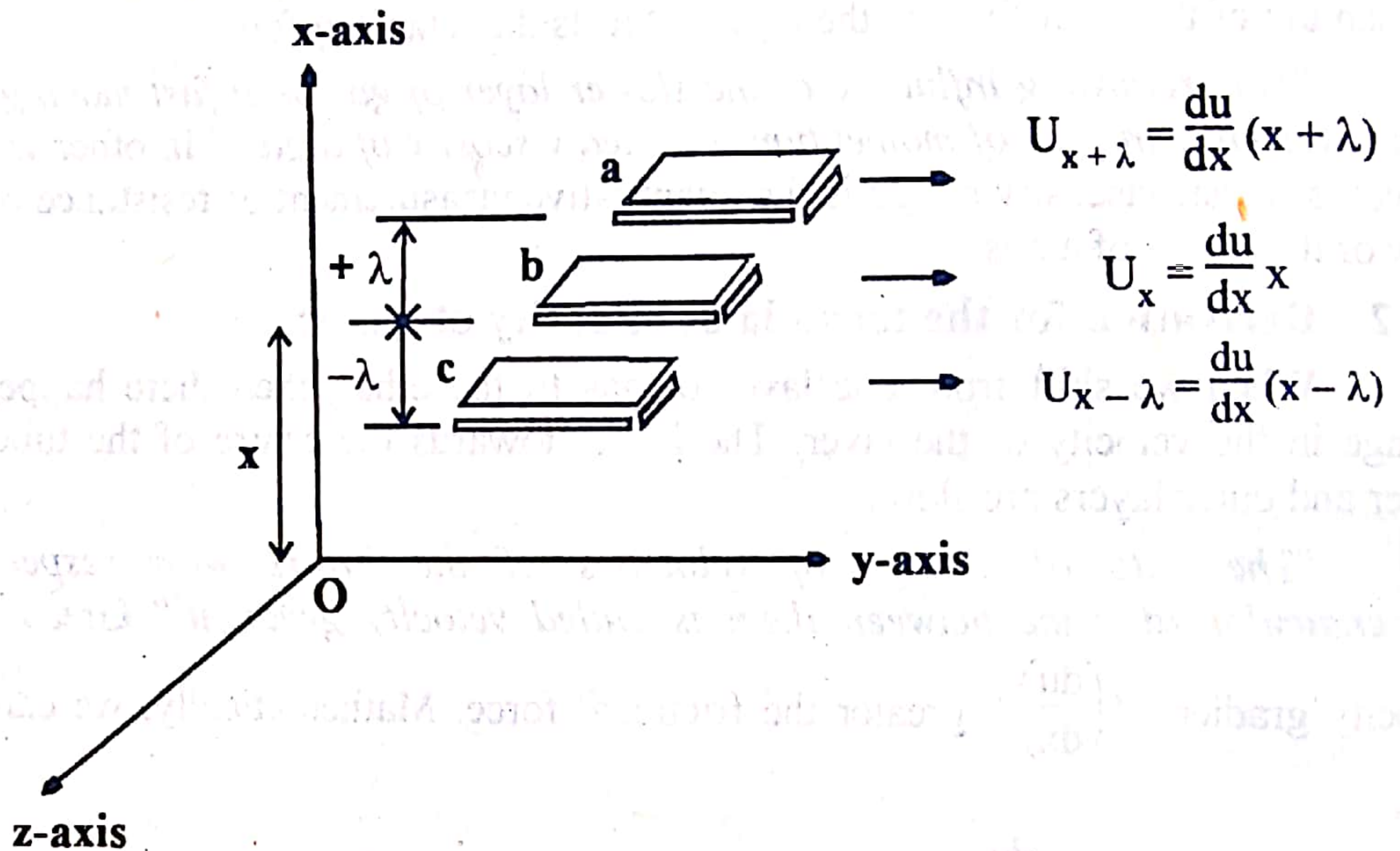
$$U_{x+\lambda} = \frac{du}{dx}(x+\lambda)$$

$$U_x = \frac{du}{dx}x$$

$$U_{x-\lambda} = \frac{du}{dx}(x-\lambda)$$

Fig. (8) Layers of a gas running parallel to Y-axis and distance between layers are along X-axis.

Now consider three layers 'a', 'b' and 'c'. Layer 'b' is at a distance 'x' from the wall of tube. The gas flows with a velocity 'u' meters per second along x-axis. The velocity gradient is $\frac{'du'}{dx}$. This means that the flow rate increases by an amount 'du' per each increment of the distance 'dx' along the x-axis perpendicular to the Y-axis.

Velocity of the layer 'b' $U_x \quad = \dfrac{du}{dx} \times x$ $\qquad$ ...... (2)

Velocity of the layer 'a' $U_{x+\lambda} = \dfrac{du}{dx} \times (x+\lambda)$ $\qquad$ ...... (3)

Velocity of the layer 'c' $U_{x-\lambda} = \dfrac{du}{dx} \times (x-\lambda)$ $\qquad$ ...... (4)

Now, suppose that a molecule of mass 'm' present in the layer 'a' transports to the layer 'b'. Momentum of the molecule in the layer 'a'.

$$mu_{(x+\lambda)} = \frac{m\,du}{dx}(x+\lambda) \qquad\qquad ...... (5)$$

Momentum of the molecule in the layer 'b' is given by equation (6)

$$mu_x = m\frac{du}{dx} \times x \qquad\qquad\qquad ...... (6)$$

If a molecule interchanges, then the rate of change of momentum in given by

$$mu_{(x+\lambda)}\downarrow - mu_x\uparrow = m\frac{du}{dx}(x+\lambda) - m\frac{du}{dx}$$

$$= m\lambda\frac{du}{dx} \qquad \cdots\cdots (7)$$

Equation (7) shows, the rate of change of momentum due to one molecule.

Now we want to calculate the number of molecules moving up and down in one second, through one 'm²' of the layer which are effective in momentum exchange. For this purpose consider the following diagram (9).
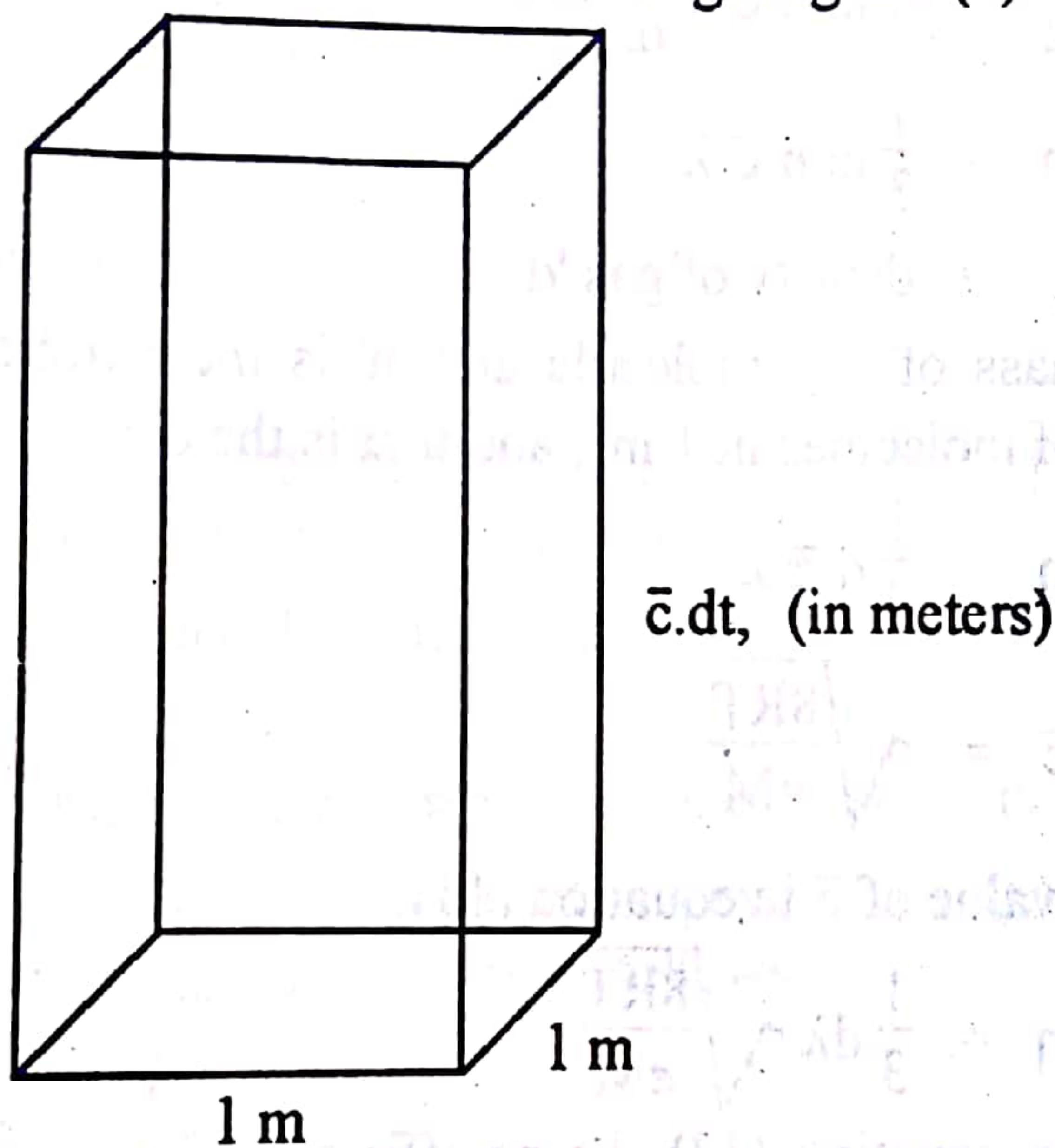
c̄.dt, (in meters)

1 m

1 m

Fig. (9)

Suppose that all the molecules are moving downward with an average velocity 'c̄', in a very short time interval dt. Each molecule travels a distance 'c̄ dt' in time interval 'dt.' Volume of the given vessel shown in diagram is,

$$\bar{c}\ dt \times 1 \times 1 = \bar{c}\ dt\ m^3$$

Suppose the number of molecules m⁻³ are 'n', then the molecules jumping from upper to the lower layer in time dt. = n c̄ dt.

In time 'dt.' seconds the number of molecule crossing $= n\ \bar{c}\ dt$

In time one second the number of molecules crossing $= \dfrac{n\ \bar{c}}{dt}\ dt = n\ \bar{c}$

It is true that out of these total molecules as n c̄, 33% are moving along x-axis 33% along y-axis and 33% along z-axis. Moreover, 50% of the molecules are moving downward and 50% upwards. It means that the number of the molecules passing to the lower layer is 50% of 33%. In other words, $\frac{1}{6}$ n c̄ will also go from lower to the higher layer. The total number of molecules exchanging momentum per second between two layers will be $= 2 \times \frac{1}{6}n\ \bar{c} = \frac{1}{3}n\ \bar{c}$ $\cdots$ (8)

Let us multiply equation (7) and (8) to get the momentum transport per second.

$$\text{Momentum transport per second} = m\,\lambda\,\frac{du}{dx} \times \frac{1}{3}\,n\,\bar{c}$$

$$= \frac{1}{3}\,m\,n\,\bar{c}\,\lambda\,\frac{du}{dx} \qquad \cdots \cdots (9)$$

This equation (9) is just equivalent to the frictional force. It should be compared with equation (1). Hence,

$$\eta\,\frac{du}{dx} = \frac{1}{3}\,m\,n\,\bar{c}\,\lambda\,\frac{du}{dx}$$

$$\eta = \frac{1}{3}\,m\,n\,\bar{c}\,\lambda \qquad \cdots \cdots (10)$$

$$m\,n = \text{density of gas 'd'}$$

'm' is the mass of one molecule and 'n' is the number of molecules m^{-3}. Hence 'mn' is mass of molecules in 1 m^3, and that is the density of gas.

$$\eta = \frac{1}{3}\,d\,\bar{c}\,\lambda \qquad \cdots \cdots (11)$$

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

Putting this value of $\bar{c}$ in equation (11),

$$\eta = \frac{1}{3}\,d\lambda\sqrt{\frac{8RT}{\pi M}} \qquad \cdots \cdots (12)$$

According to equation (12) the co-efficient of viscosity depends upon the density of the gas, mean free path, temperature and molar mass of gas.

Let us rearrange equation (12) to get the value of λ.

$$\lambda = \frac{3\eta}{d\sqrt{\dfrac{8RT}{\pi M}}} \qquad \cdots \cdots (13)$$

So, mean free path is directly proportional to the co-efficient of viscosity and inversely proportional to the density and temperature of the gas. If we substitute the average velocity in equation (13) by root mean square velocity, then

$$\lambda = \frac{3\eta}{0.921\,d\sqrt{\dfrac{3RT}{M}}} \qquad \cdots \cdots (14)$$

EXAMPLE (5)

The viscosity of hydrogen at 0°C is 8.41×10^{-6} kg m^{-1} s^{-1}. Calculate the mean free path of H_2 at S.T.P.

SOLUTION:

Data:

$$T = 0\,°C + 273 = 273\,°K, \quad R = 8.3143\,J\,K^{-1}\,mol^{-1}$$

$$\eta = 8.41 \times 10^{-6}\,kg\,m^{-1}\,s^{-1}$$

First of all we calculate the density of H_2.

Since 1 mole of H_2 at S.T.P $= 22.414 \text{ dm}^3 = 0.024414 \text{ m}^3$

Molar mass of $H_2 = 2 \times 10^{-3} \text{ kg mol}^{-1}$

$$d = \frac{\text{mass}}{\text{volume}} = \frac{2 \times 10^{-3} \text{ kg}}{0.0224 \text{ cm}^3} = 8.93 \times 10^{-2} \text{ kg m}^{-3}$$

The expression for average velocity is,

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}, \quad \bar{c} = \sqrt{\frac{8 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}{3.14 \times 2 \times 10^{-3} \text{ kg mol}^{-1}}}$$

$$= 1.70 \times 10^3 \text{ ms}^{-1}$$

The formula for mean free path (λ) is

$$\lambda = \frac{3\eta}{\bar{c} d}$$

By putting the values

$$\lambda = \frac{3 \times 8.41 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}}{1.70 \times 10^{-3} \text{ ms}^{-1} \times 8.93 \times 10^{-2} \text{ kg m}^{-3}} = \boxed{1.67 \times 10^{-7} \text{ m}} \text{ Ans.}$$

It means that one molecule is at a distance of 1.67×10^{-7} m from the other in this vessel.

1.6.4 Effect of pressure and temperature on viscosity of a gas:

The formula for the co-efficient of viscosity of a gas, density of the gas, mean free path and the average velocity is as follows.

$$\eta = \frac{1}{3} d \bar{c} \lambda \qquad \cdots \cdots (11)$$

Since, $\quad d = \dfrac{Mn}{N_A} \qquad \left(\text{Since } \dfrac{M}{N_A} = m \text{ and } m\,n = d \right)$

$$\lambda = \frac{1}{\sqrt{2}\, \pi \sigma^2\, n}$$

and $\quad \bar{c} = \sqrt{\dfrac{8RT}{\pi M}}$

Putting these parameter in equation (11), we get the following expression

$$\eta = \frac{1}{3} \frac{Mn}{N_A} \frac{1}{\sqrt{2\pi}\, \sigma^2\, n} \sqrt{\frac{8RT}{\pi M}}$$

$$\eta = \frac{\sqrt{8}}{3\sqrt{2}} \frac{M}{N_A \sigma^2 \pi} \sqrt{\frac{RT}{\pi M}} = \frac{2}{3} \frac{1}{N_A \pi \sigma^2} \sqrt{\frac{MRT}{\pi}}$$

$$\eta = \frac{2}{3} \frac{1}{N_A \pi \sigma^2} \sqrt{\frac{MRT}{\pi}} \qquad \cdots \cdots (15)$$

This equation (15) tells us that the viscosity of an ideal gas is independent of the pressure. It is directly proportional to the square root of absolute temperature. It is inversely proportional to the square of the collision diameter.

1.6.5 Reason for the effect of temperature on viscosity of a gas:

According to the kinetic molecular theory of gases, the molecules of a gas move randomly and they migrate from one layer of the gas to the other layer. When the temperature is increased, then the rate of transport of the momentum between the streaming and stationary layers increases. This thing increases the viscosity of the gas.

This behavior is in contradiction to the effect of temperature on viscosities of liquids. In the cause of liquids, the viscosities decrease due to decreasing forces of attraction among the molecules of a liquid.

1.6.6 Effect of temperature and pressure on mean free path:

The molecules of the gases are very small and the sizes of the collision diameters vary in the range 2×10^{-10} m to 4×10^{-10} m. It means that the mean free path will not vary greatly from one gas to another. The reason is that, at normal temperature and pressure a molecule of a gas is approximately 300 times away from the other molecule, than its own diameter. It means that the product of 'n' and 'λ' is approximately constant.

$$\lambda = \frac{1}{\sqrt{2}\,\pi\,\sigma^2 n}$$

$$n\lambda = \frac{1}{\sqrt{2}\,\pi\,\sigma^2}$$

In the above consideration, all the factors in the denominator of right hand side are constants. So, 'nλ' is constant

$$n\lambda = \text{constant} \qquad \cdots\cdots (1)$$

We also know that at constant pressure the number of molecules 'n' in unit volume is inversely proportional to the temperature $\left(PV = nRT; \ n = \dfrac{PV}{RT}\right)$.

Hence, we can say that

$$n \propto \frac{1}{T} \qquad \cdots\cdots (2)$$

So, substituting 'n' by 'T'

$$\frac{\lambda}{T} = \text{constant} \quad \text{(if pressure in constant)}.$$

If the temperature is changed from T_1 to T_2, then, the mean free path should change from 'λ_1', to 'λ_2'..

$$\frac{\lambda_1}{T_1} = \frac{\lambda_2}{T_2} = \text{constant} \qquad \cdots\cdots (3) \ \text{(when pressure is constant)}$$

Number of molecules per unit volume is directly proportional to pressure.

$$n \propto P \qquad \cdots\cdots (4)$$

Putting this in equation (1)

$$P\lambda = \text{constant (when the temperature is constant)}$$

Similarly, we can say that,

$$P_1\lambda_1 = P_2\lambda_2 \qquad \ldots\ldots (5)$$

If gas is maintained at ordinary temperature and pressure, then the value of λ for most of the gases is, 10^{-7} m. It means that

$$10^{-7}\ m \times P = \text{constant}$$

If we want to make the mean free path of a gas as one meter, then the pressure should be 10^{-7} atm. In other words, we can say that the pressure of 10^{-5} atm. is required to have a mean free path of 1 cm.

These calculations are helping us to have an idea that the farness or nearness of gas molecules can be imagined at various conditions of pressure.

1.6.7 Measurement of a viscosity of a gas:

Principle:

The viscosity of a gas can be determined by measuring the rate of flow of the gas through a cylindrical tube of known internal diameter.

Poiseuille equation is used

$$\eta = \frac{\pi(P_1 - P_2)\, r\, t}{8\, v l}$$

where

t = time taken for the volume v to pass through the capillary tube

l = length of capillary tube

r = radius of capillary tube

P_1 and P_2 = pressures at two ends of the tube

All the terms except 'η' and 't' can be kept constant. So, following equation can be used by taking a reference in addition to that gas, which is under study. The equation is as follows:

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2}$$

or

$$\frac{\eta_{(gas)}}{\eta_{(ref)}} = \frac{t_{(gas)}}{t_{(ref)}}$$

Apparatus:

This apparatus was invented by Rankine in 1910 and is shown in the following diagram (10).

It is consisted of a closed circuit formed by a bent capillary tube having diameter 0.2 mm on the left side. The diameter of the right tube is 3 mm.

A small pellet of Hg is entrapped in a wider tube. The apparatus is cleaned and filled with a gas at 1 atm. pressure. The tube is inverted in order to bring the pellet above the mark 'A'. The apparatus is placed in a constant temperature bath and the time is noted for the Hg pellet to travel from 'A' to 'B'.

Actually, this is the time which is taken by the gas to travel through the capillary tube under definite pressure gradient provided by the Hg pellet. Under the similar conditions, the time of flow for the reference gas is determined. Applying the above equation, the $\eta_{(gas)}$ is calculated.
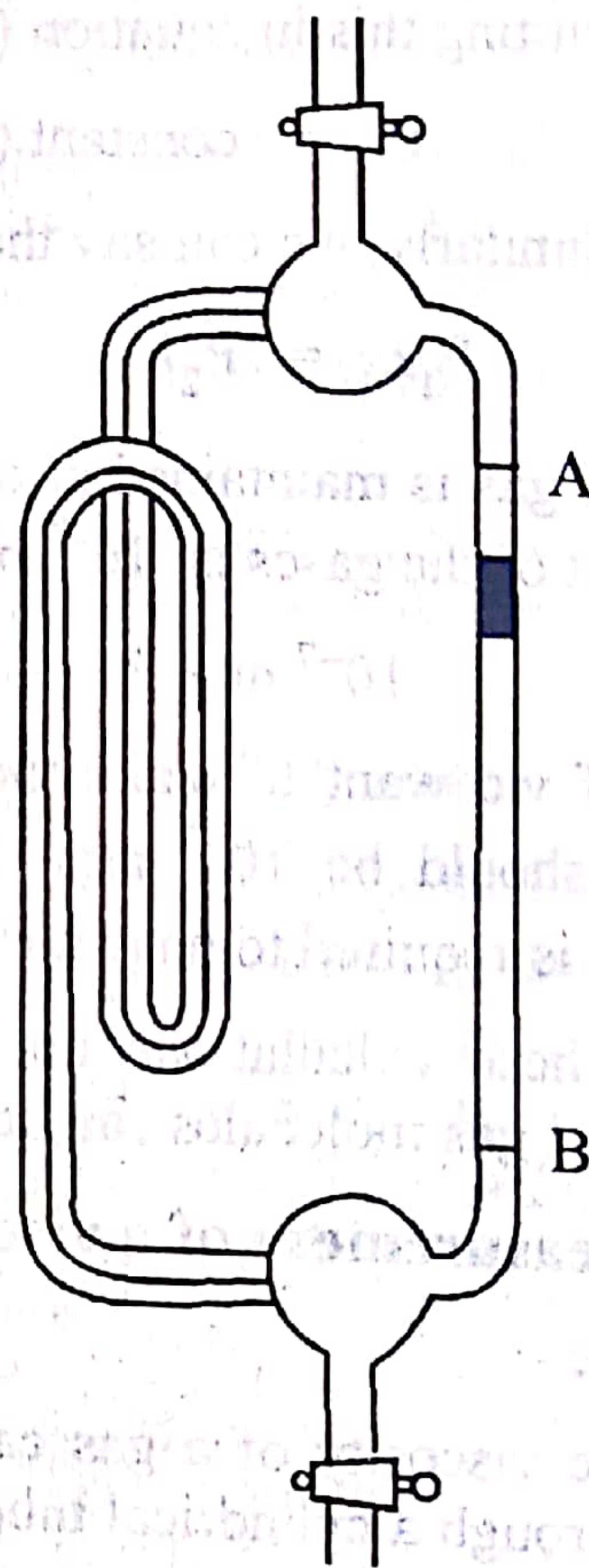

Fig. (10) Rankine apparatus for measuring the viscosity of a gas.

The following table (2) gives the values of co-efficient of viscosities for some of the gases.

Table: (2) Co-efficients of viscosity of various gases

Gases	Temperature, K	$10^4 \, \eta$, (P)
Nitrogen	298	1.78
Oxygen	298	2.08
Hydrogen	298	0.90
Argon	298	2.27
Water (vapour)	298	0.98
Carbon monoxide	298	1.76
Carbon dioxide	298	1.50
Helium	298	1.97
Mercury (vap.)	298	2.50
Hydrogen chloride	298	1.33
Hydrogen bromide	298	1.171
Hydrogen iodide	298	1.73

1.7.0 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 (11). It means that the product of P and V does not remain constant, at constant temperature.
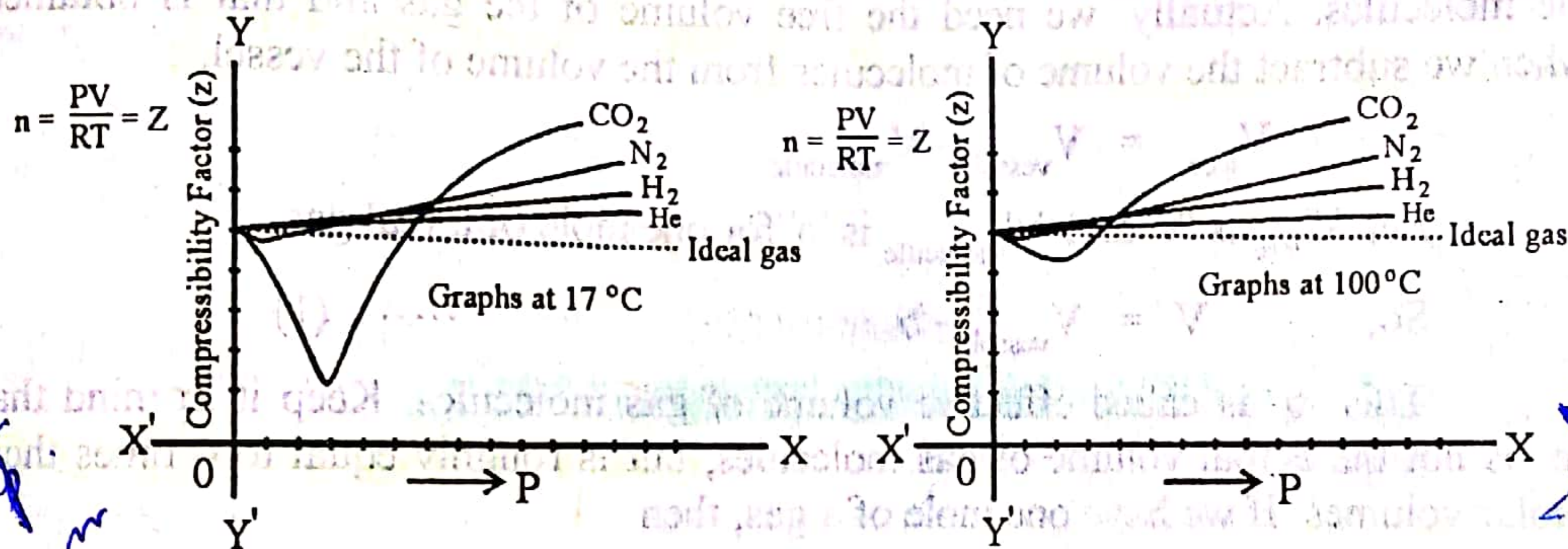
$n = \dfrac{PV}{RT} = Z$

Compressibility Factor (z)

CO₂
N₂
H₂
He
Ideal gas

Graphs at 17 °C

$n = \dfrac{PV}{RT} = Z$

Compressibility Factor (z)

CO₂
N₂
H₂
He
Ideal gas

Graphs at 100°C

Ideal
high temp
low pressure

Non-ideal
Low temp
High pressure

Fig. (11) *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.

1.7.1 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.

1.7.2 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, $$V = V_{vessel} - b \qquad \ldots\ldots (1)$$

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 $\dfrac{a}{V^2}$.

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

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 = attraction per unit volume for a particular gas.

'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.

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

For 'n' moles of a gas,

$$\left(P + \frac{an^2}{V^2} \right)(V - nb) = nRT \qquad \cdots\cdots (4)$$

Van der Waal's Constant!

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

1.7.3   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 (3). 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:

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

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

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

1.7.4 Van der Waal's constants for some important gases:

Since H_2 and He are non-polar gases so, their 'a' factors are sufficiently smaller than many other gases. CO_2 and NH_3 are big sized molecules and so their 'a' factors are sufficiently high. 'b' factor is the measurement of volume of gas molecules in closest possible positions of molecules. This factor is also significant for CO_2, NH_3 and CH_4.

When we say that, the value of the 'b' factor for H_2 is 0.02661 dm^3 $mole^{-1}$, then it means that it is 26.61 cm^3 mol^{-1}. In other words, we can say that,

one mole of H_2, i.e., 2.016 grams will occupy a volume of 26.61 cm³ when the molecule are very very close to each other in the gaseous state. It means that, calculated volume of H_2 gas is 26.61 cm³.

1.7.5 Prove that b = 4V$_m$:

According to kinetic molecular theory of gases an individual molecule in a gas occupies no volume. But actually molecules of real gases have finite sizes. So the available free space for their motion may be less than the total volume of the container. The space which is occupied by a molecule at an instant will not be available to other molecules at the same instant for its motion. It means that every molecule excludes the certain volume for all other molecules.

In order to illustrate it, suppose that a molecule of a gas is non-compressible. It is a spherical particle of radius 'R'. When two molecules are at closest approach to each other, then their centres are separated by '2R', as shown in the following diagram (12).
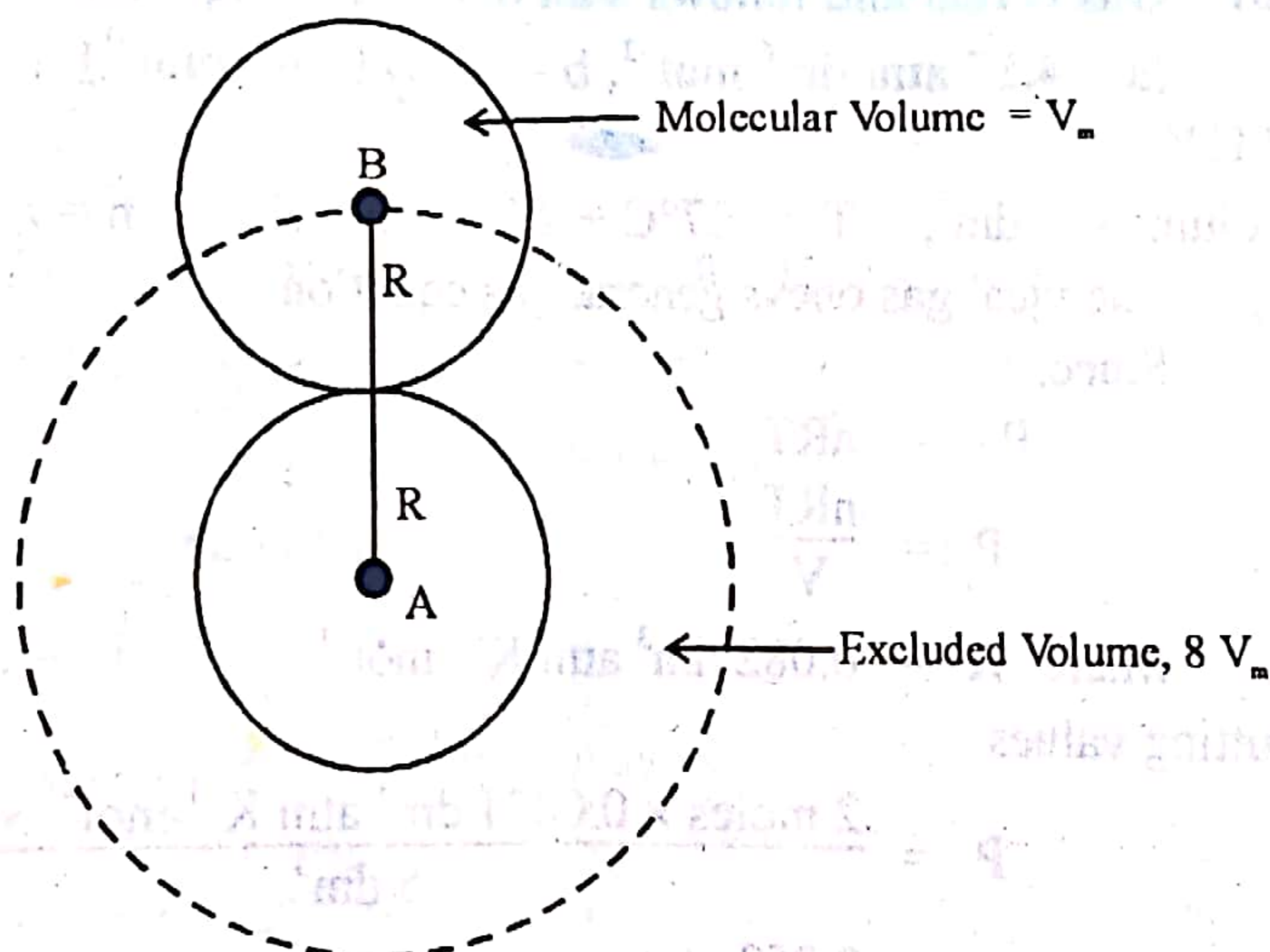

Fig. (12) Concept of excluded volume.

The molecule 'A' excludes the centre of the molecule 'B' to be present in a space equal to the volume of dotted sphere. The volume of this sphere with dotted lines is

$$\frac{4}{3} \cdot \pi \, (2R)^3 = 8 \times \frac{4}{3} \, \pi \, R^3$$

In the same manner, the molecule B also excludes centre of the molecule 'A' from a space equal to $8 \times \frac{4}{3} \, \pi \, R^3$. When the two molecules are closest approach, then they mutually exclude a volume $8 \times \frac{4}{3} \, \pi \, R^3$.

The volume excluded by one molecule is half of this volume and that is

$$4 \times \frac{4}{3} \, \pi \, R^3.$$

Since, the volume of one molecule is $= \frac{4}{3} . \pi . R^3$, so volume excluded by one molecule = four times the above volume. Now, if we have one mole of gas which has Avogadro's number of molecules, then

$$b = 4N_A \left(\frac{4}{3} \pi R^3 \right) \quad \text{= one molecul}$$

Now $\qquad N_A \left(\frac{4}{3} \pi R^3 \right) = V_m \quad \text{= one mole}$

Hence $\qquad b = 4V_m.$

This 'b' is called excluded volume, effective volume or vibratory volume.

EXAMPLE (6)

Two moles of NH_3 were found to occupy a volume of 5 dm³ at 27°C. Calculate the pressure,

   (i)   If gas behaves ideally
   (ii) Gas is real and follows Van der Waal's equation.
         (a = 4.17 atm dm⁶ mol⁻², b = 0.0371 dm³ mol⁻¹)

SOLUTION:

Volume = 5 dm³, $\quad$ T = 27°C + 273 = 300K $\qquad$ n = 2 moles

   (i)   The ideal gas obeys general gas equation
         Since,

$$PV = nRT$$

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

where R = 0.082 dm³ atm K⁻¹ mol⁻¹
Putting values

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

$$= 9.852 \text{ atm.}$$

   (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

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

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

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

1.7.6 Validity of Van der Waal's equation:

While we have discussed the non-polar behaviour of gases by graphical explanation, it was noticed that some of the gases have lower values of $\frac{PV}{RT} = Z$, than expectations at low 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 $\quad Z = 1 - \frac{a}{RTV} \qquad \cdots\cdots (7)$

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.

(iii)   At extremely low pressure:

At very low pressure, we say that the pressure approaches to zero. In this way, 'V' becomes very large. Under there circumstances, the term Pb, $\frac{a}{V}$ and $\frac{ab}{V^2}$ would become negligible and can be ignored relative to 'RT'. Thus equation (5) is converted to,

$$PV = RT$$

It means that at very very low pressures, the real gases behave ideally.

(iv)   At high temperature:

When the temperature of the real gas is very high, then volume would be very large. In other words, 'P' will be small. The terms like 'Pb' $\frac{a}{V}$ and $\frac{ab}{V^2}$ can be ignored. Equation (5) reduces to,

$$PV = RT$$

It means that at high temperature, the real gases behave ideally.

(v)   Exceptional behaviour of H_2 and He:

H_2 and He are very small sized molecules and they are non-polar in nature.

They have least attractive forces. Their 'a' factor is very small, so $\frac{a}{V}$ and $\frac{ab}{V^2}$ in equation (5) can be ignored. Hence equation (5) can be written as

$$PV = RT + Pb$$

Dividing by 'RT'

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

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

It means 'Z' is always greater than 1. Graphs for H_2 and He also show that the curves for hydrogen lie above the ideal curve.

1.8.0 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 (13) 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.
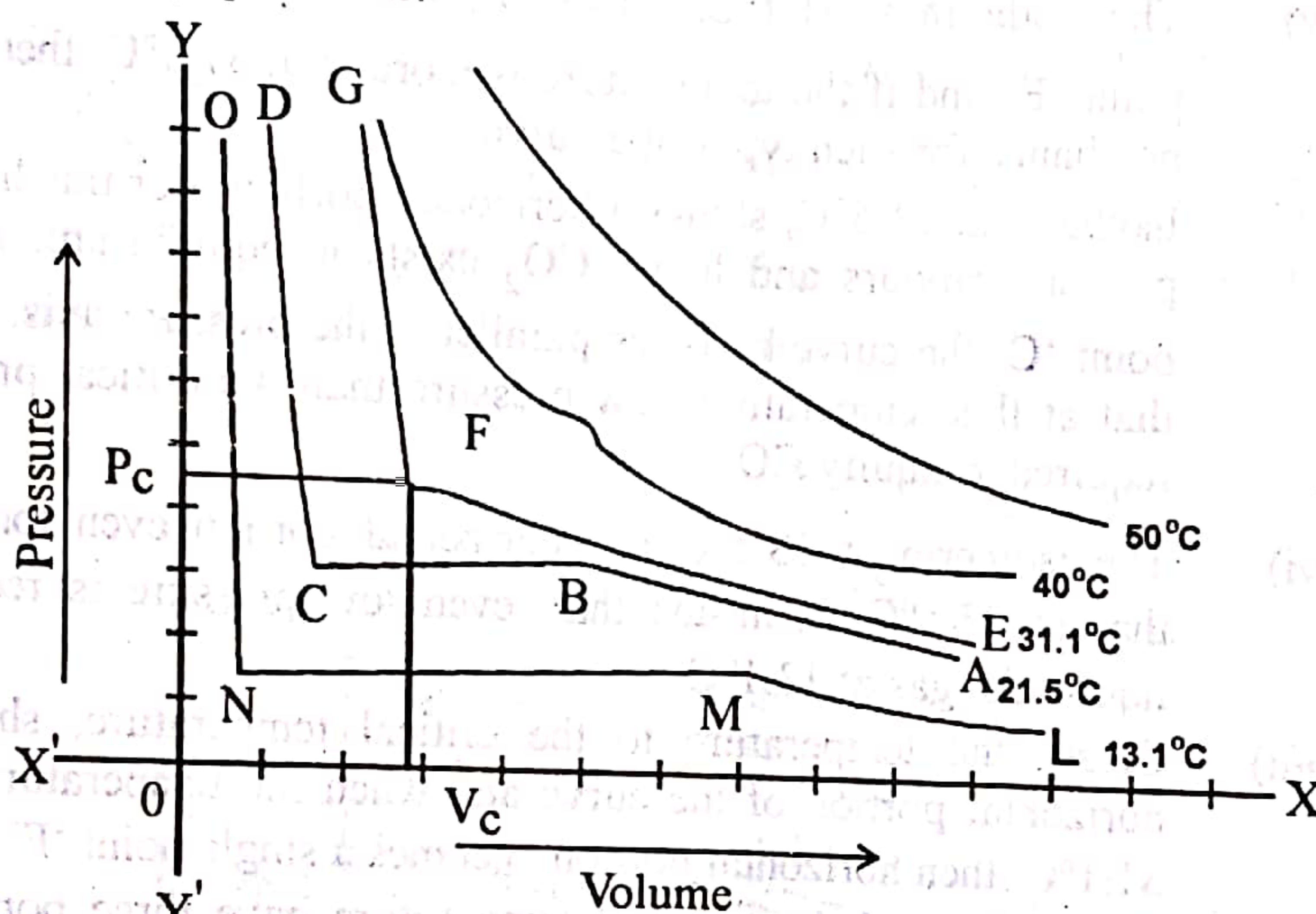

Fig. (13) Isotherms of one mole of CO_2 at various temperatures and idea of critical temperature of gases.

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.

1.8.1 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.

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

Open the brackets on L.H.S.

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

Multiplying by 'V^2' and dividing by 'P' and rearranging we get

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

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

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. (14). 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 (14) is obtained.
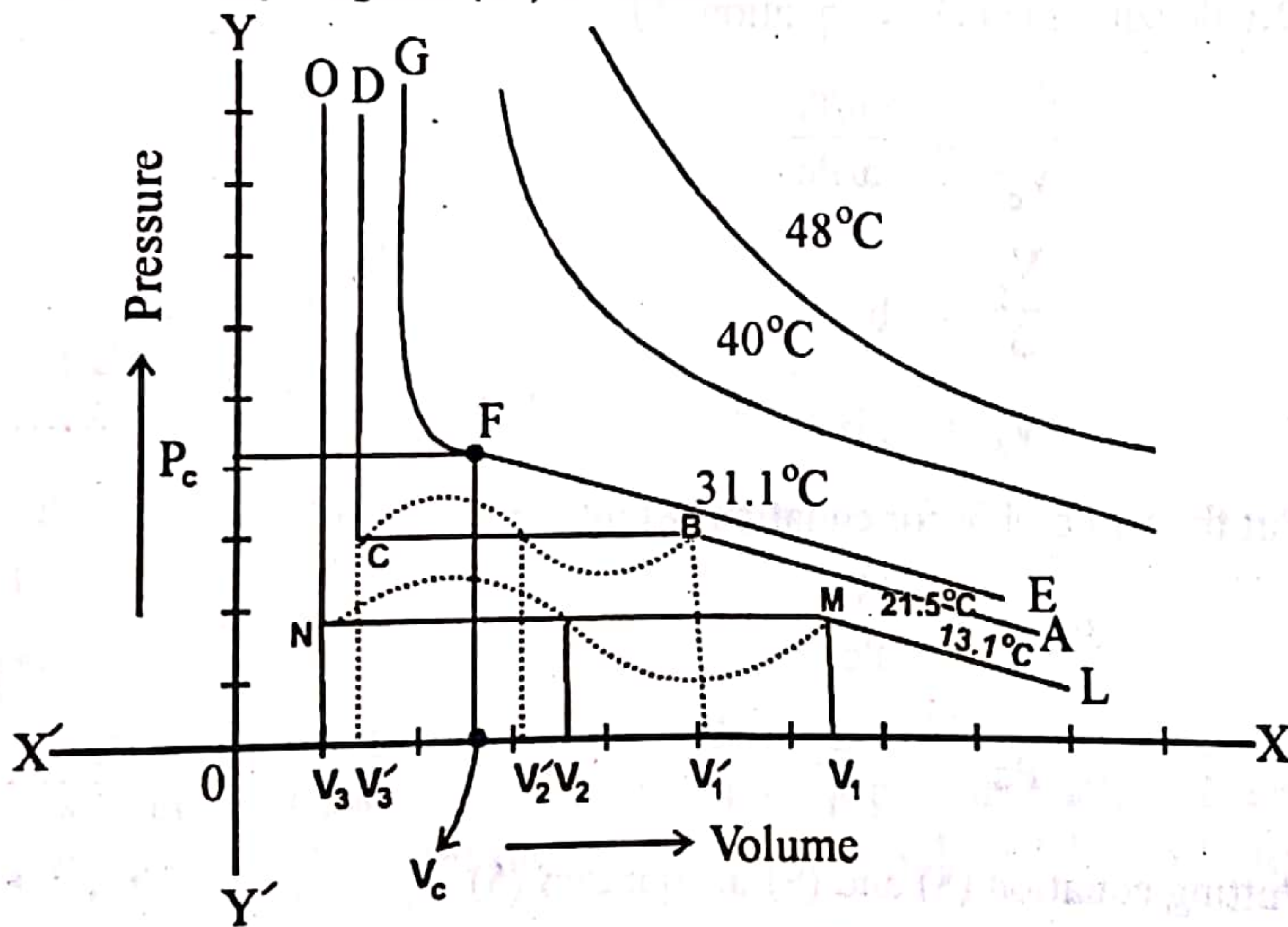

Fig. (14) Comparison of isotherms of CO_2 above and below critical temperature.

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

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.

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

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

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

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, $\quad V_c \quad = \quad 3b$

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

Since $\quad \dfrac{a}{P_c} \quad = \quad 3V^2_c$ ...... (6)

So $\quad \boxed{a \quad = \quad 3P_c V_c^2}$ ...... (12)

We know that for one mole of an ideal gas

$$PV = RT$$

$$\therefore \qquad R = \frac{PV}{T}$$

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

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

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

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

EXAMPLE (7)

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:

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

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

Calculation of critical volume

Since $\quad V_c = 3b$

Putting value of 'b'

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

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

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,

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

$T_C = \boxed{305.1 \text{ K}}$ Ans.

EXAMPLE (8)

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

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,

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

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

Since, $b = \dfrac{RT_C}{8 P_C}$

Putting values,

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

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

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

1.8.2 Experimental determination of critical temperature:

Critical temperature is determined with the help of Cagniard de la tour's apparatus. It is consisted of hard glass U-tube blown into a bulb at the lower end. The bulb is surrounded by jacket. The liquid whose critical temperature and pressure is required is placed in the bulb and the rest of tube is filled with mercury. The upper end of the U-tube is sealed leaving a little air in it. This arrangement will help to act it as a manometer. The temperature of the bulb containing the liquid is raised slowly by the heating jacket. A point is reached when the meniscus of the liquid becomes faint. Then it disappears. It shows that the distinction between liquid and vapour is not possible. Following diagram makes the idea clear. Fig. (15).
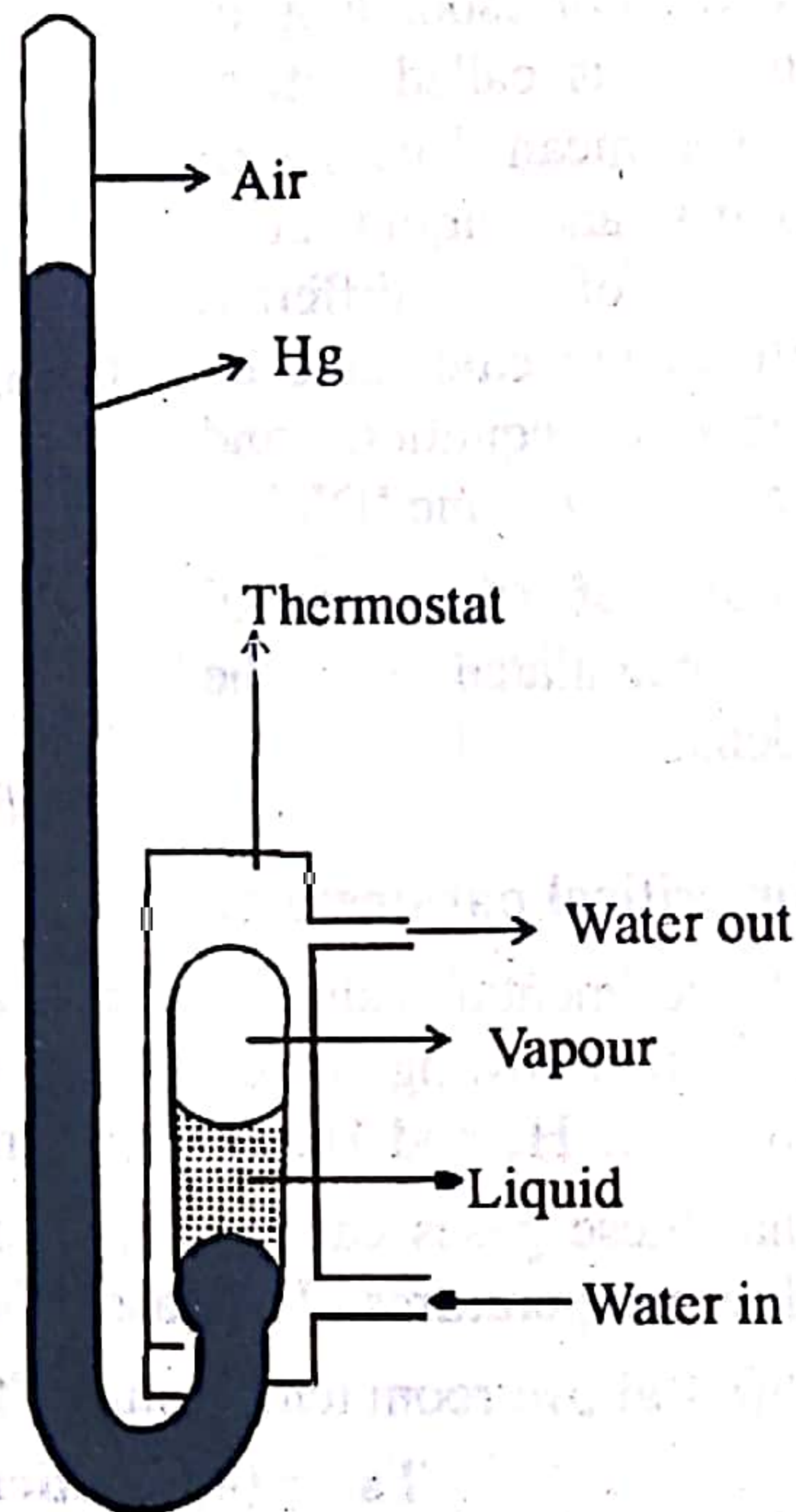

Fig. (15) Determination of critical temperature by cagniard de la Tour's apparatus.

That temperature is recorded at which the meniscus disappears. The bulb is allowed to cool again. First of all a mist is formed in the gas which quickly settles with the appearance of the meniscus. That temperature at which the meniscus reappears is noted. Then the mean of these two temperatures is calculated which is the critical temperature of the liquid.

Critical pressure:

The pressure which is recorded on the manometer at the critical temperature, is called critical pressure.

1.8.3 Determination of critical volume:

The determination of critical volume is based upon the rule of Cailletet and Mathias. This rule says that, the mean value of the densities of liquid and saturated vapours for any stable substance is linear function of temperature.

The densities of a liquid and its vapours at a number of temperatures near the critical point are noted. These densities are plotted against the temperature. Graph shown in the fig. (16) is obtained. The portion 'X', 'Y', of the graph is for saturated vapours and the portion 'YZ' is for liquid. The curves meet at the point 'Y'.

The density corresponding to the point 'Y' is called critical density. The mean densities of the vapours and liquid at a number of different temperatures are calculated by the following equation and they give a straight line 'DY'.

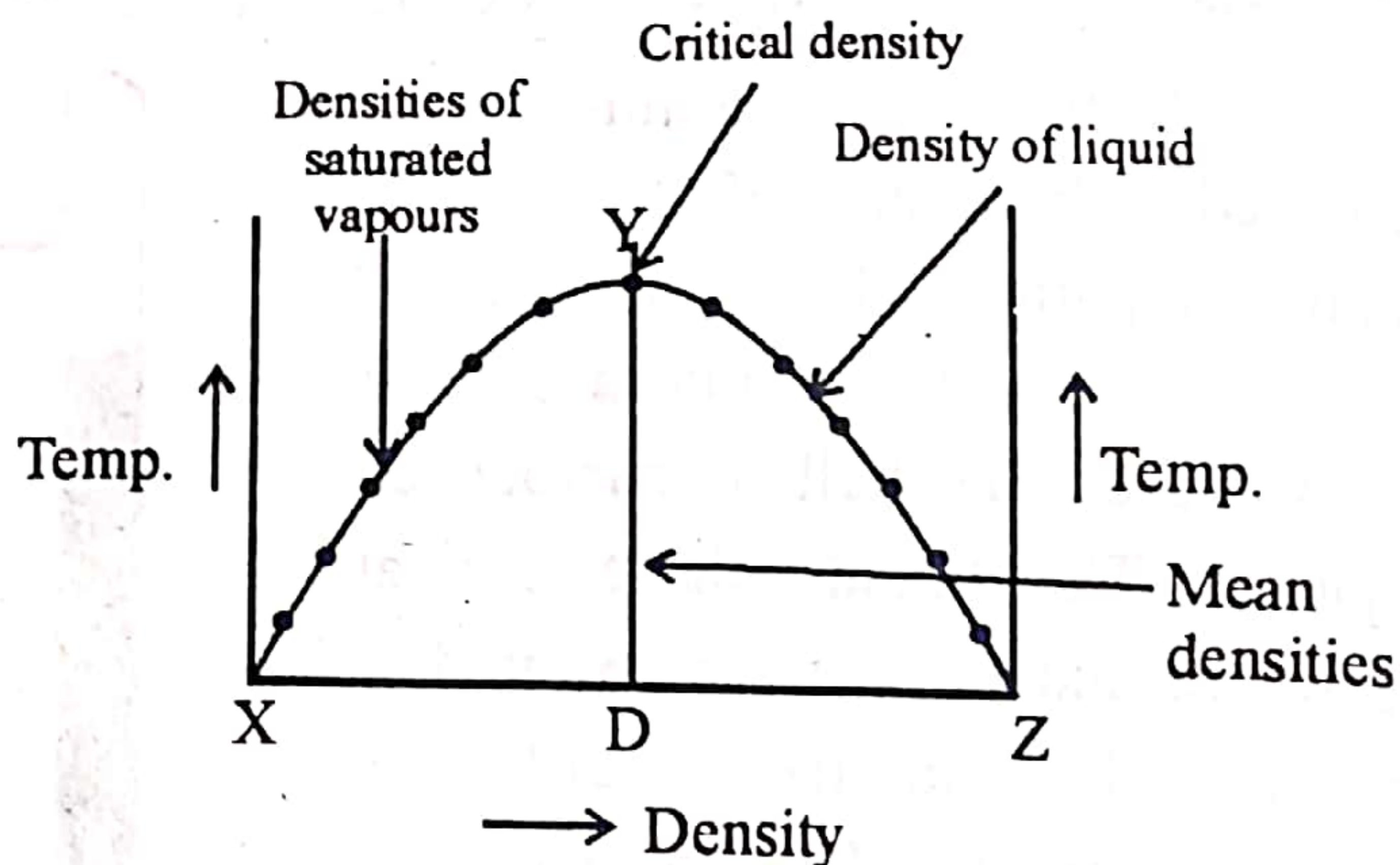The value of the critical volume is calculated from the critical density.

Fig. (16) Determination of critical volume.

Table for critical parameters:

Experimental values of critical temperature, pressure and volume are shown in the following table (4). As it is clear from the table, that the critical temperatures of H_2 and He are very small and they are close to absolute zero. It means that these gases can be liquefied by increasing pressures by bringing them to very low temperatures. The gases like HCl, NH_3, Cl_2 and SO_2 have the critical temperatures above room temperature. It means that their liquefaction is easier.

Table (4) Critical constants of gases

Gases	Critical temperature T_c (°K)	Critical pressure P_c (atm.)	Critical Volume V_c (cm³)
Helium (He)	5.2	2.26	60.68
Hydrogen (H_2)	33.2	12.28	64.51
Nitrogen (N_2)	126.0	33.5	90.03
Carbon monoxide (CO)	134.4	34.6	90.03
Argon (Ar)	150.7	48.2	78.43
Oxygen (O_2)	154.3	49.7	74.42
Methane (CH_4)	190.2	45.6	98.76
Carbon dioxide (CO_2)	304.3	72.2	95.65
Nitrous oxide (N_2O)	306.9	71.9	96.91
Hydrochloric acid (HCl)	324.5	81.6	89.90
Hydrogen sulphide (H_2S)	373.5	89.0	126.86
Ammonia (NH_3)	405.5	111.5	72.03
Chlorine (Cl_2)	417.1	76.1	123.91
Sulphur dioxide (SO_2)	430.3	77.6	124.75

1.8.4 Law of corresponding states:

When we plot the isotherm of CO_2, then we know that isotherm above the critical temperature are parabolic curves. If we have different gases then the isotherms close to their critical temperatures are of same type, but these critical isotherms do not coincide with each other. The reason is that, the values of the Van der Waal's constants 'a' and 'b' are different for different gases.

If the individual gases are studied under the conditions of such temperatures and pressures which are same fractions of critical temperature and pressure, then these values of pressure, volume and temperature are the ratios of these values,

$$P_r = \frac{P}{P_c}$$

$$V_r = \frac{V}{V_c}$$

$$T_r = \frac{T}{T_c}$$

'P_r', 'V_r' and 'T_r' are called reduced pressure, reduced volume and reduced temperature respectively. It means that the critical isotherms of various gases will coincide with each other, if they are maintained at same reduced parameters. In order to explain the reduced parameters for different gases, we have to manage them at such 'P', 'V' and 'T' values, that when these values are divided by their critical parameters then the ratios should be same for all the gases:

Since $P_r = \dfrac{P}{P_c}$ so, $P = P_r P_c$

As $V_r = \dfrac{V}{V_c}$ so, $V = V_r V_c$ $\left.\right\}$ ...... (1)

and $T_r = \dfrac{T}{T_c}$ so $T = T_r T_c$

Van der Waal's equation for one mole of gas is

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

Let us put the values of 'P', 'V' and 'T' from the set of equations (1) in equation (2)

$$\left(P_r P_c + \frac{a}{V_r^2 V_c^2}\right)(V_r V_c - b) = R(T_r \cdot T_c) \qquad \cdots (3)$$

We know that the critical parameter have been expressed in terms of Van der Waal's constant as follows.

$$\left.\begin{array}{l} P_c = \dfrac{a}{27b^2} \\[2mm] V_c = 3b \\[2mm] T_c = \dfrac{8a}{27Rb} \end{array}\right\} \qquad \cdots\cdots (4)$$

Putting these values of $'P_c'$, $'V_c'$ and $'T_c'$ in equation (3), we get the following relationship,

$$\left(P_r \cdot \frac{a}{27b^2} + \frac{a}{9V_r^2 b^2}\right)(3V_r \cdot b - b) = R.T_r \frac{8a}{27Rb} \qquad \cdots\cdots (5)$$

Taking some factors as common

$$\frac{a}{27b^2}\left(P_r + \frac{3}{V_r^2}\right) \cdot b(3V_r - 1) = 8\frac{a}{27b} \cdot T_r$$

The simplified equation will be as follows:

$$\left(P_r + \frac{3}{V_r^2}\right).(3V_r - 1) = 8T_r \qquad \cdots\cdots (6)$$

This equation (6) is called Van der Waal's reduced equation of state. When we compare this equation with Van der Waal's equation (2), then we see that the factors like 'a', 'b', $'P_c'$ and $'T_c'$ are eliminated. These factors are characteristic parameters of different gases. When they are not present in the equation (6) then it is applicable to all substances in the liquid and gaseous state irrespective of their specific nature.

According to equation (6), if any two or more substances have the same reduced pressure $'P_r'$, and they are maintained at same reduced temperature T_r, then they will have same reduced volume $'V_r'$. Those substances which are under these conditions are said to be in the corresponding states. This statement is called law of corresponding states.

1.8.5 Applications of law of corresponding states:

An important application of law of corresponding states is that we construct a single diagram and this diagram gives 'P', 'V', 'T' relationship for all gases. In order to construct the diagram, we plot a graph between reduced pressure $'P_r'$ on x-axis and compressibility factor $'\dfrac{PV}{RT} = Z'$ on y-axis.

For an ideal gas 'Z' is unity. The real gases show the deviation from this unity. The compressibility falter 'Z' gives us the quantitative measurement of deviation of a gas from ideal behaviour. It is observed that, if various gases are maintained at such temperatures, that the $'T_r'$ values of all the gases is 2, and then

we plot a graph between 'P$_r$' and 'Z', a graph very close to the straight line is obtained. It means that all these gases are very close to the ideal behaviour.

When the temperature of these gases are such that the 'T$_r$' values are 1.5, 1.2, and 1.1, then minimum position in the curves are obtained and when the 'T$_r$' is unity, then it means that temperatures of these gases are equal to the critical temperatures. Gases become maximum non-ideal and they are liquefied. It appears from the curves, that the gases with same values of reduced variables will show similar departure from ideality. Following graph (17) makes the idea clear.
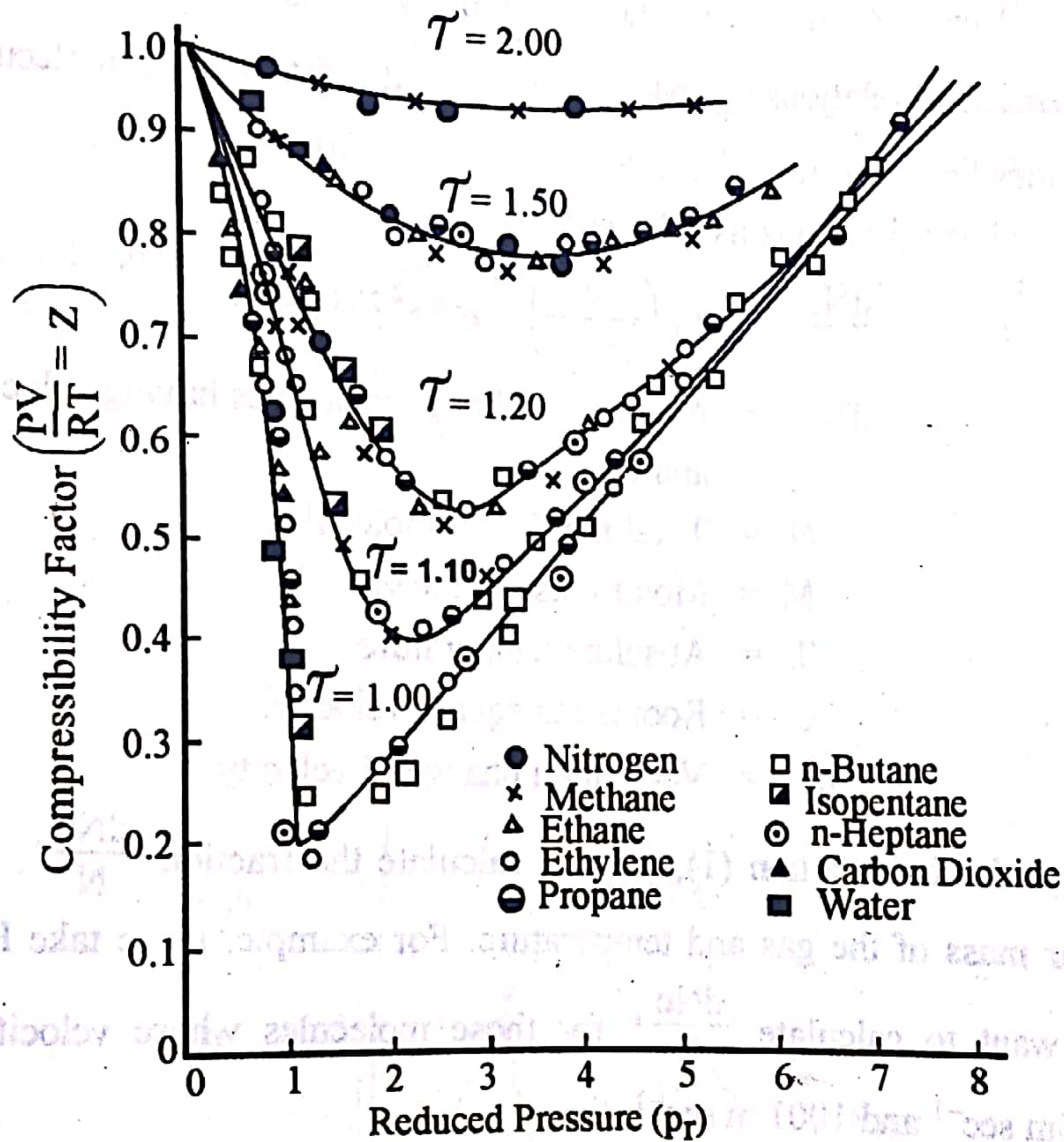

Fig (17). *Compressibility factor $\frac{PV}{RT}$ as a function of reduced variables.*

1.9.0 DISTRIBUTION OF MOLECULAR VELOCITIES

According to kinetic theory of gases, molecules of a gas move randomly, collide among themselves, collide with the walls of the vessel and change their directions. During the collisions, they exchange the energies and change the velocities. If we keep an eye on one of the molecules of a gas, then its velocity and energy changes million of times per second. For this reason, we have to talk about the root mean square velocity or average velocity of gas molecules.

If the temperature is constant for the gas, then we can calculate that majority of the molecules have the velocities close to the average velocity. A fewer molecules have velocities very high or very low than the average velocity.

It is not possible that we follow each molecule and come to know about its velocity. It is reasonable to choose the molecules having velocities in a certain velocity range.

Suppose we have a gas consisting of 'N' molecules. These molecules are moving with a constant root mean square velocity, 'c'. When the temperature is constant then a fraction of molecules will have a definite velocity range. Suppose we have 'dN' molecules out of total 'N', which have a velocity between c and c + dc, where 'dc' is a very small change of velocity:

Keeping in view the probability considerations, Maxwell gave a mathematical relationship which gives us the fraction of molecules $\dfrac{dN}{N}$ whose velocities lie between 'c' and 'c + dc'.

The equation is as follows:

$$\frac{dN_c}{N} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mc^2/2RT} c^2\, dc \qquad \cdots\cdots (1)$$

dN_c = A small number of molecules having velocity between c and c + dc

N = Total number of molecules

M = Molar mass of the gas

T = Absolute temperature

c = Root mean square velocity.

dc = Very small change of velocity

In the equation (1), we can calculate the fraction '$\dfrac{dN_c}{N}$', if we know the molar mass of the gas and temperature. For example, if we take H_2 gas at 27°C, and want to calculate '$\dfrac{dN_c}{N}$' for those molecules whose velocities lie between 1000m sec^{-1} and 1001 m sec^{-1}, then

M = 2.018 g mol^{-1} = 2.018 × 10^{-3} kg mol^{-1}

T = 27 + 273 = 300 K

c = 1000 m sec^{-1}.

dc = 1 m sec^{-1}.

Putting these values, we can come to know that what is the part of the total molecules which have velocities in this range.

Equation (1) can be written as follows:

$$\frac{1}{dc}\cdot\frac{dN_c}{N} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mc^2/2RT} c^2 \qquad \cdots\cdots (2)$$

The L.H.S of this equation (2) i.e. '$\dfrac{1}{dc}\cdot\dfrac{dN_c}{N}$', represents the probability of finding the molecules with the velocity 'c' and 'c + dc'.

1.9.1 Graphical representation of Maxwell's law:

If we plot a graph between velocities of molecules an x-axis and the L.H.S of equation (2) on y-axis, then a curve is obtained showing the maxima.

Following diagram (18) shows that the Maxwell's curve at 0°C starts from zero velocity and its fraction is very close to zero. The curve shows a peak then falls and goes along the velocity axis. It means that at this temperature, there are certain molecules with very high velocities, but their fraction become very low. The velocity corresponding to the peak of the curve is possessed by the greatest fraction of the molecules. Remember that, this velocity is not possessed by greatest number of molecules. This velocity is called most probable velocity.

The area below the curve, give us the total number of molecules 'N'.

1.9.2 Effect of temperature on distribution of velocities:

If the H_2 gas is maintained at 25°C (298 K) rather than 0°C, then the Maxwell curve lowers its peak and shifts to the higher velocities. Those molecules which have low velocities than most probable, reduce their fractions
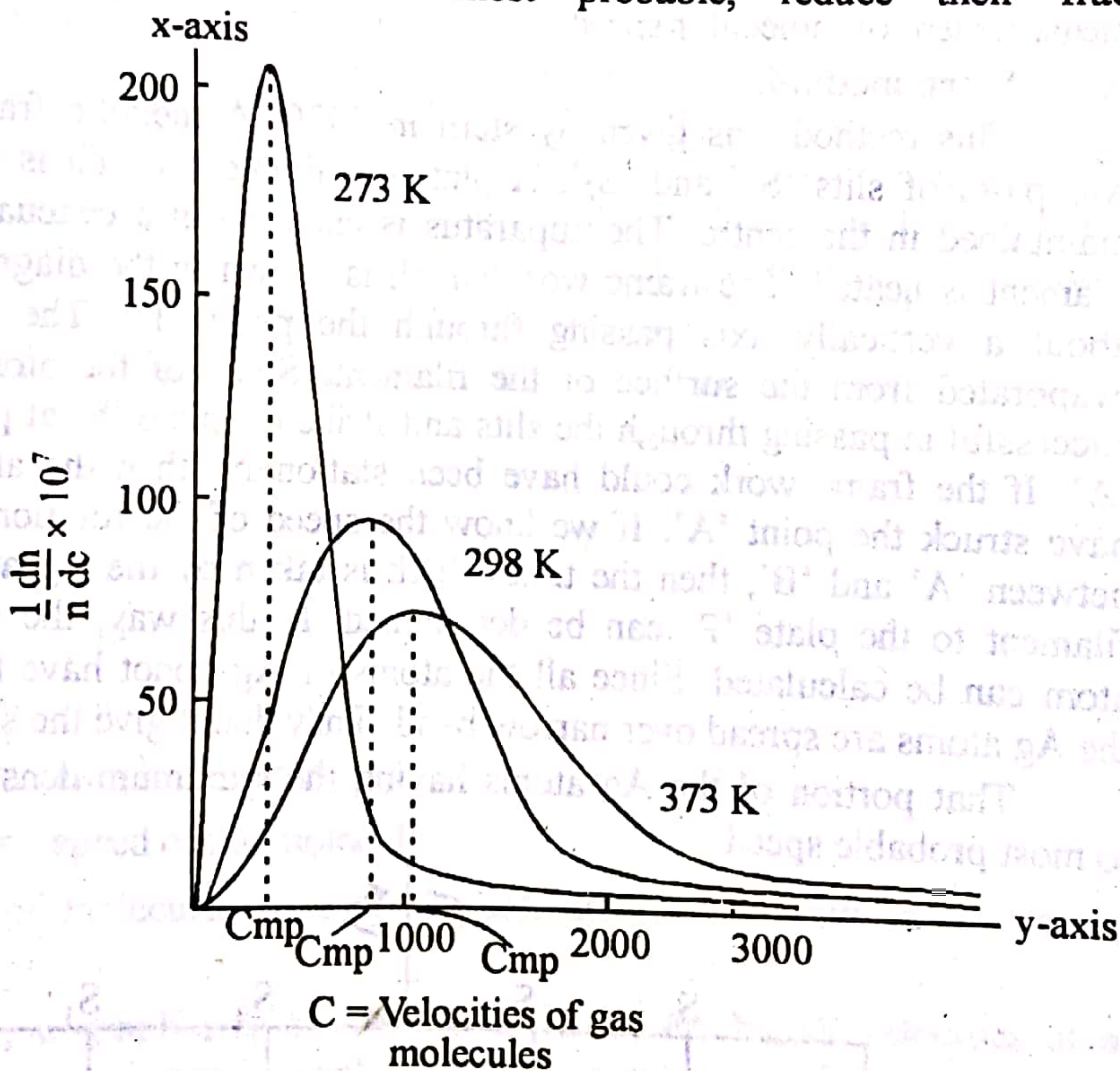

Fig. (18) Maxwell's curves for distribution of velocities of different temperatures.

and the molecules having velocities greater than the most probable increase the variety of fractions. Simply, we can say that, there happens a wider distribution of velocities at higher temperature.

The area under the curve at 298 K remains uneffected. Similarly, the curves at 373 K (100 C°) shows even greater distribution of velocities.

If the temperature is decreased say upto 0°C, then the maximum on the distribution curve is shifted towards the y-axis.

Distribution of velocities and the reaction rates:

As explained above, the increase of temperature creates greater distribution of velocities. The fraction of molecules having greater velocities and energies increase. So, the number of fruitful collisions increase. This thing makes the reactions faster.

1.9.3 Derivation of most probable velocity:

Most probable velocity can be obtained for any gas by two ways.

(i)   By doing the calculations theoretically, plotting a graph and looking at the most probable velocity in front of the peak.

(ii)   The equation (2) is differentiated with respect to 'c' and put it equal to zero. Actually at the peak of the curve, the slope of point is zero and whenever the slope is zero, then it means that rate of change of dependent variable with respect to independent variable is zero.

1.9.4 Experimental determination of molecular speeds:

Mostly there are two methods which are generally employed for the measurement of molecular speed.

1.   Stern method:

This method was given by stern in 1920. A metallic frame work contains two pairs of slits 'S_1' and 'S_2'. A platinum filament which is coated with Ag is maintained in the centre. The apparatus is enclosed in a evacuated vessel and the filament is heated. The frame work which is shown in the diagram (19) is rotated about a vertically axis passing through the point 'F'. The atoms of Ag are evaporated from the surface of the filament. Some of the atoms of Ag become successful in passing through the slits and strike the plate 'P' at point 'B' but not at 'A'. If the frame work could have been stationary, then the atoms of Ag would have struck the point 'A'. If we know the speed of the rotation, and the distance between 'A' and 'B', then the time which is taken by the Ag atom to travel from filament to the plate 'P' can be determined. In this way, the velocity of the Ag atom can be calculated. Since all the atoms of Ag donot have the same speed, so the Ag atoms are spread over narrow band. They donot give the sharp line.

That portion of the Ag atoms having the maximum density will correspond to most probable speed.
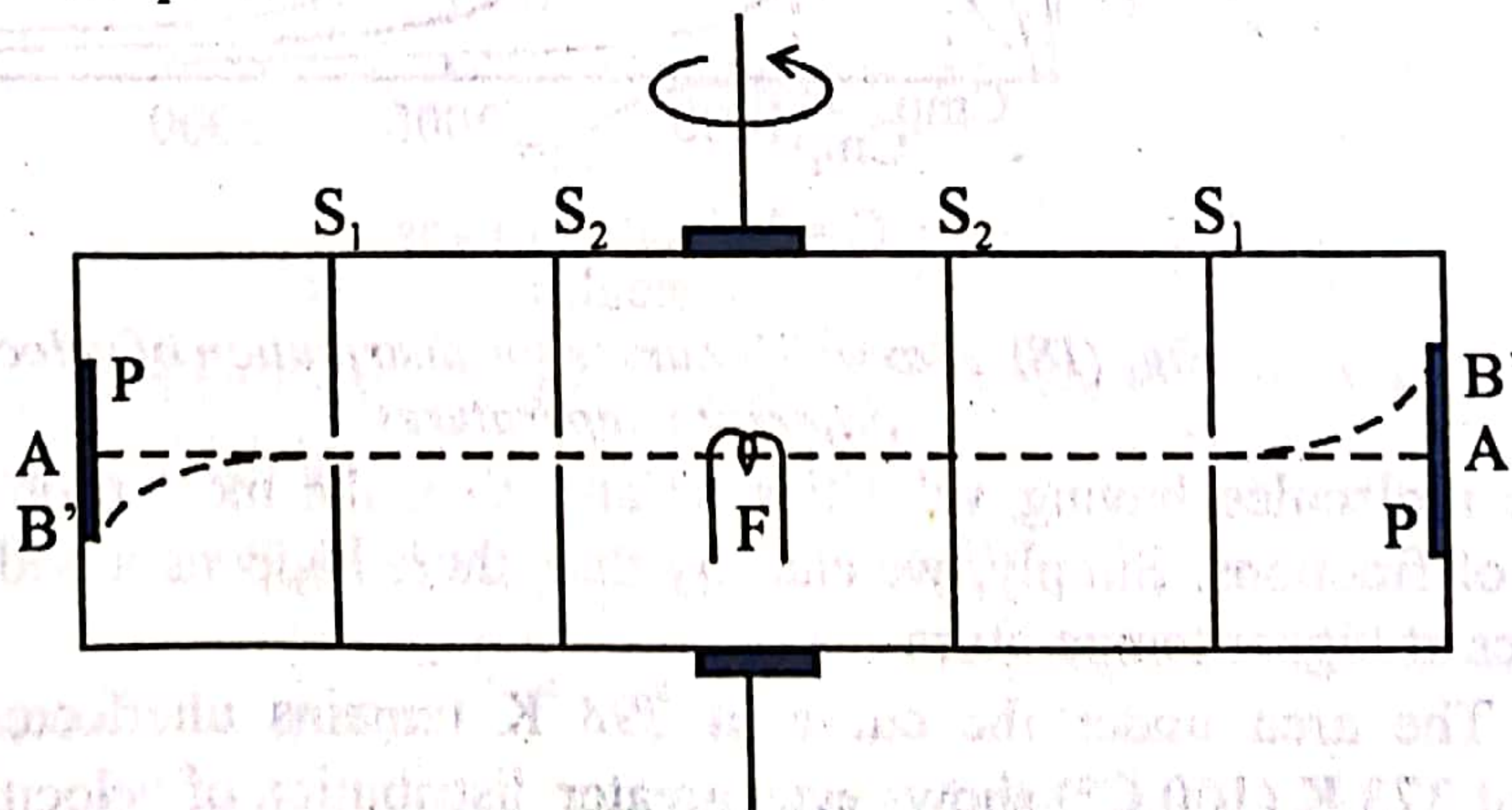

Fig. (19) A two dimensional view of the apparatus employed by
Stern for measuring the molecular speeds.

2. **Lammert's speed filter method:**

This method was evolved in 1927 and it was direct experimental proof of Maxwell's law. The apparatus is shown as the following diagram (20):
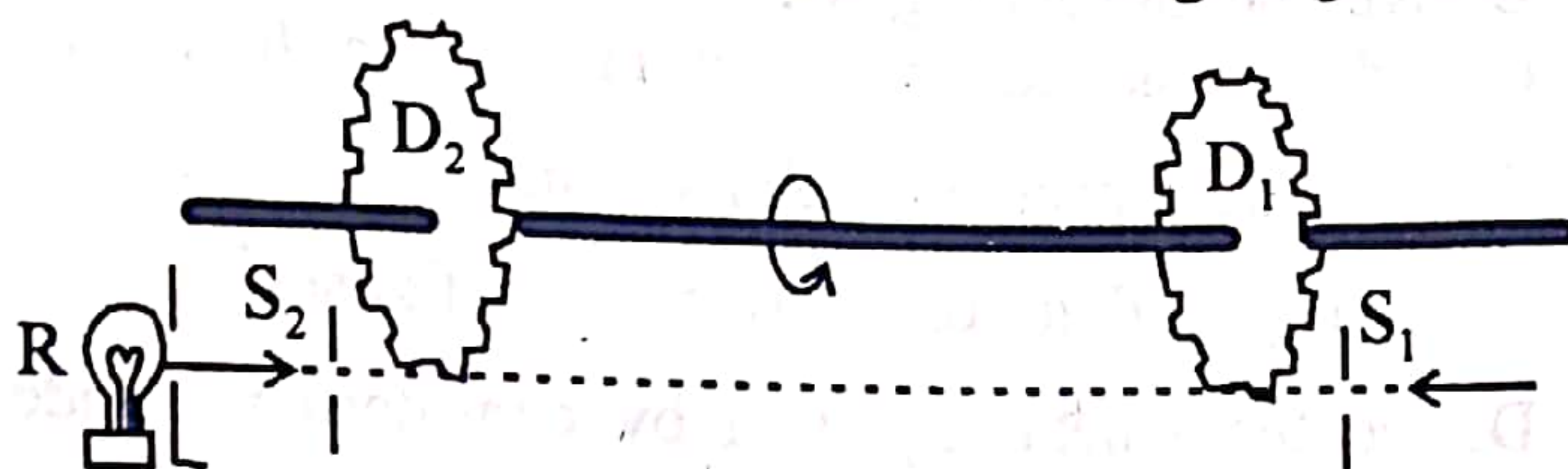

Fig. (20) The apparatus used in Lammert's speed filter method.

There are two discs which are slotted. They are mounted on a common axis 'A'. The discs can rotate at the speed of 500 – 600 rotation per minute. During rotation the slots in 'D₁' and 'D₂' are exactly in line.

A sensitive radiometer is placed, which can measure the angular diffraction and hence the intensity of the molecular beam. This apparatus is kept in an evacuated chamber. When the discs are stationary, then the molecule of the gas passing through 'D₁' can also pass through. 'D₂' and recorded by radiometer. Now, the slotted discs are rotated at high speed. A molecule which passes through a gap in 'D₁' will pass through a gap in 'D₂' only if the time required by the molecule to cover the distance between the discs is equal to an integral multiple of time. This time is required for the discs to rotate from one slot to the next.

Following equation is used to measure the velocity of the molecule

$$\text{nu} = \frac{ad\omega}{2\pi}$$

Where, n = small integer

a = number of slots in each disc

d = distance between the discs

ω = angular velocity of the disc

u = speed of the molecule

The number of molecules passing through are given by the deflection of radiometer vanes.

In this way, a graph is plotted from lower to the higher velocities at a particular temperature, and most probable velocity is calculated from the peak of the curve.