(iii) *A gas mixture of 3 litre of Propane (C_3H_8) and Butane (C_4H_{10}) on complete combustion at 25°C produced 10 L CO_2. What is the composition of gas mixture, i.e., vol. of C_3H_8* and *C_4H_{10}* respectively ?

(A) 1.5 L, 1.5 L **(B)** 1 L, 2 L **(C)** 2 L, 1.0 L **(D)** 1.75 L, 1.25 L

(iv) *40.0 mL of gaseous mixture of CO and C_2H_2 is mixed with 100.0 mL of O_2 and burnt. The volume of the gas after the combustion is 105 mL. Calculate the composition of the original mixture :*

(A) 25 mL of CO and 15 mL of C_2H_2 **(B)** 15 mL of CO and 25 mL of C_2H_2
(C) 10 mL of CO and 30 mL of C_2H_2 **(D)** 20 mL of CO and 20 mL of C_2H_2

(v) *When 100 mL sample of methane and ethane along with excess of O_2 is subjected to electric spark, the contraction in volume was observed to be 212 mL. When the resulting gases were passed through KOH solution, further contraction in volume was :*

(A) 60 mL **(B)** 96 mL **(C)** 108 mL **(D)** None of these

KINETIC MOLECULAR MODEL OF A GAS — Section - 3

In the previous sections, we have studied the macroscopic properties of gases and their relationships in the form of gas laws. Now, we know that for a given amount of gas, volume is directly proportional to the absolute temperature but gas laws do not provide any reason for this.

To understand the underlying principles, a theory based on a model is proposed. If the theoretical results on the basis of this particular model agree with the experimental observations, it indicates that the model is realistic. The theory that provides an explanation for the various experimental observations about a gas is based on the **Kinetic Molecular Model**.

Maxwell proposed the postulates for the behavior of gas molecules known as **Kinetic Theory of gases**.

The postulates of this model are :

- Each gas is made up of a large number of identical and small (tiny) particles known as molecules (i.e., the dimensions of these molecules are very-very small as compared to the space between them).
- The volume of a molecule is so small that it may be neglected in comparison to the total volume occupied by the gas.
- There are practically no attractive forces between the molecules. Thus, the molecules move independently.
- The molecules are never in stationary state but are believed to be in random motion in a straight line motion in all possible directions with altogether different but constant velocities. The direction of motion is changed only when it collides with the walls of container or with other molecules.
- The molecules are perfectly elastic and bear no change in energy during collisions.
- The effect of gravity on molecular motion is negligible.
- The temperature of gas is the measure of its kinetic energy. K.E. of molecules is proportional to absolute temperature of the gas.
- The pressure of the gas is due to the continuous collision of molecules on the walls of container.

Consider a container of volume V occupied by a gas.

Let m = mass of the gas in the container and N = number of molecules in the container

If m_o is the mass of one molecule $\Rightarrow$ $m = m_o N$

If N_o is the Avogadro number and M is the molecular weight of the gas,

$\Rightarrow$ $M = m_o N_o$

Root mean Square (C_{rms}) speed :

It is defined as : $c_{rms} = \sqrt{\overline{c^2}} = \sqrt{\dfrac{c_1^2 + c_2^2 + c_3^2 + \ldots\ldots\ldots + c_N^2}{N}}$

[where bar $\left(\overline{}\right)$ represents average $\Rightarrow$ $\overline{c^2}$ = Average of c^2 values]

Since the distribution is continuous, we can write : $c_{rms}^2 = \overline{c^2} = \dfrac{\int c^2\, dN_c}{N} = \dfrac{3k_B T}{m} \equiv \dfrac{3RT}{M_o}$

Where M_o = Mol. mass of the gas (in Kg)

$\Rightarrow$ $c_{rms} = \sqrt{\dfrac{3RT}{M_o}}$

Note : Derivation of the above integrals is not required.

Illustrating the concept:

The escape velocity, the velocity required by an object to escape from the gravitational field of earth, is given by $c_e = \sqrt{2gr}$ where r = 6400 km for earth. At what temperature will the c_{rms} of an H_2 molecule attain escape velocity ? ($g = 10\ ms^{-2}$)

$$c_e = \sqrt{2 \times 10 \times 6400 \times 10^3} = 11313.7\ ms^{-1}$$

$$c_{rms} = \sqrt{\frac{3RT}{M_o}} = \sqrt{\frac{3 \times 8.314 \times T}{2 \times 10^{-3}}} \quad [\text{Note : } M_{H_2} = 2 \times 10^{-3}\ kg\ ]$$

As $c_{rms} = c_e$ $\Rightarrow$ $T = 10263.8\ K$

Average speed (c_{avg}) :

This is defined as : $c_{avg} = \bar{c} = \dfrac{c_1 + c_2 + c_3 + \ldots.. + c_N}{N}$

For a continuous distribution, it can be written as : $c_{avg} = \dfrac{\int c\, dN_c}{N} = \sqrt{\dfrac{8RT}{\pi M_o}}$

Note : This is actually "average speed". Since, the molecule move randomly, average velocity of the gas is zero.

Illustrating the concept:

The average speed of a gas molecule is 400 m/s. Calculate its rms velocity at the same temperature.

$$c_{rms} = \sqrt{\frac{3RT}{M}} \text{ and } c_{avg} = \sqrt{\frac{8RT}{\pi M}} \Rightarrow c_{rms} = \sqrt{\frac{3\pi}{8}} \times 400\ ms^{-1} = 434.24\ ms^{-1}$$

Most Probable speed (C_{MP}) :

A very small fraction of molecules occupy either very small or very high speeds. The speed occupied by majority of molecules is known as most probable speed.

It is given by : $c_{MP} = \sqrt{\dfrac{2RT}{M_o}}$

Illustrating the concept:

For a gas consisting of only six molecular having speeds as $2\,ms^{-1}$, $3\,ms^{-1}$, $3\,ms^{-1}$, $3\,ms^{-1}$, $4\,ms^{-1}$, $5\,ms^{-1}$, find c_{rms}, c_{avg} and c_{MP}.

$$c_{avg} = \bar{c} \equiv \frac{\sum_{i=1}^{N} c_i}{N} \equiv \frac{c_1 + c_2 + \ldots + c_N}{N} = \frac{2+3+3+3+4+5}{6} = 3.33\,ms^{-1}$$

$$c_{rms} = \sqrt{\overline{c^2}} \equiv \sqrt{\frac{\sum_{i=1}^{N} {c_i}^2}{N}} \equiv \sqrt{\frac{{c_1}^2 + {c_2}^2 + \ldots + {c_N}^2}{N}} = \sqrt{\frac{2^2 + 3^2 + 3^2 + 3^2 + 4^2 + 5^2}{6}} = 3.46\ ms^{-1}$$

$c_{MP} = 3\,ms^{-1}$ (Since maximum numbers of molecules are having a speed of 3 ms^{-1})

Note :

(i) $c_{MP} < c_{avg} < c_{rms}$

$$c_{MP} : c_{avg} : c_{rms} :: \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$1 : 1.128 : 1.224$$

Also, $c_{avg} = c_{rms} \times 0.9215$

(ii) c_{avg} and c_{rms} values lie in the vicinities of c_{MP} values.

(iii) The numerical values of c_{MP}, c_{avg}, c_{rms} increases with increase in temperature.

(iv) Also, it is important to note that the average translational kinetic energy of a gas molecule is given by :

$$K.E_{avg} = \frac{1}{2} m_o c_{rms}^2 \neq \frac{1}{2} m_o c_{avg}^2$$

If in a gas, there are N molecules, their total K.E. is :

$$K.E_{Total} = K.E_1 + K.E_2 + \ldots + K.E_N = \frac{1}{2} m_o c_1^2 + \frac{1}{2} m_o c_2^2 + \ldots + \frac{1}{2} m_o c_N^2$$

Thus, average kinetic energy of each molecule

$$= \frac{\frac{1}{2} m_o c_1^2 + \frac{1}{2} m_o c_2^2 + \ldots. + \frac{1}{2} m_o c_N^2}{N}$$

$$= \frac{1}{2} m_o \left(\frac{c_1^2 + c_2^2 + \ldots. + c_N^2}{N} \right)$$

$$= \frac{1}{2} m_o c_{rms}^2$$

(v) The sharpness of maximum in curves decreases with increase in temperature which reveals that number of molecules having speeds in the vicinities of c_{MP} increase.

Kinetic Energy of Gas

The pressure exerted by the gas is :

$$P = \frac{1}{3}\frac{m_o N}{V} c_{rms}^2 \quad \text{or} \quad P = \frac{1}{3}\rho c_{rms}^2 \quad \text{where } \rho = \text{density of gas} = \frac{m_o N}{V}$$

Using the above relation and gas laws, a relation between the average translational kinetic energy $\left(\frac{1}{2} m_o c_{rms}^2\right)$ of a molecule at the temperature, T of the gas can be derived.

Using PV = nRT

$$\Rightarrow \quad \frac{1}{3}\frac{m_o N}{V} c_{rms}^2 V = \frac{N}{N_o} RT \qquad \left[\text{Using } P = \frac{1}{3}\frac{m_o N}{V} C_{rms}^2\right]$$

Note : $K.E_{avg.} = \frac{1}{2} m_o c_{rms}^2 \neq \frac{1}{2} m_o c_{avg}^2 \qquad \left[\because \frac{c_1^2 + c_2^2 + \ldots + c_N^2}{N} \neq \left(\frac{c_1 + c_2 + \ldots + c_N}{N}\right)^2\right]$

or $\quad \frac{1}{3} m_o c_{rms}^2 = \frac{1}{N_o} RT$

$$\Rightarrow \quad \frac{1}{2} m_o c_{rms}^2 = \frac{3}{2}\frac{RT}{N_o} = \frac{3}{2} k_B T$$

$\Rightarrow$ Average Translational K.E. of a molecule is directly proportional to the temperature of the gas.

$K.E_{avg} = \frac{3}{2} k_B T \qquad$ [where $k_B = \frac{R}{N_o}$ is known as Boltzmann constant]

Also, $K.E./mole = \frac{3}{2} PV = \frac{3}{2} RT$

Illustration - 13 *Find the temperature at which methane and ethane will have the same rms speed as carbon dioxide at 400°C. Also calculate the mean velocity and most probable velocity of methane molecules at 400°C.*

SOLUTION :

$$c_{rms} = \sqrt{\frac{3RT}{M_o}}$$

Let 1: CO_2 and 2: Methane

For c_{rms} to be same for 1 and 2

$$\Rightarrow \quad \frac{T_1}{M_1} = \frac{T_2}{M_2}$$

(a) $T_{CH_4} = \frac{673}{44} \times 16 = 244.73K$

(b) $T_{C_2H_6} = \frac{673}{44} \times 30 = 458.86K$

Mean speed (CH_4) $= \sqrt{\frac{8RT}{\pi M_o}} = \sqrt{\frac{8 \times 8.31 \times 673}{3.14 \times 16 \times 10^{-3}}} = 943.68$ m/s

Most probable speed (CH_4) $= \sqrt{\frac{2RT}{M_o}} = \sqrt{\frac{2 \times 8.31 \times 673}{16 \times 10^{-3}}}$

$= 836.11$ m/s

Illustration - 14 *A gas bulb of 1 L capacity contains* 2.0×10^{21} *molecules of nitrogen exerting a pressure of* 7.57×10^3 Nm^{-2}*. Calculate the root mean square (rms) speed and the temperature of the gas molecules. The ratio of the most probable speed to the root mean square speed is* 0.82*, calculate the most probable speed for these molecules at this temperature.*

SOLUTION :

$$c_{rms} = \sqrt{\frac{3RT}{M_o}} \quad T = ?$$

Using, $PV = nRT$

$$\Rightarrow \quad T = \frac{PV}{nR} = \frac{7.57\times10^3\times1\times10^{-3}}{\frac{2.0\times10^{21}}{6.023\times10^{23}}\times8.314} = 274.2\text{ K}$$

$$c_{rms} = \sqrt{\frac{3\times8.314\times274.2}{28\times10^{-3}}} = 494.22\text{ m/s}$$

$$\text{Most probable speed } (c_{MP}) = \frac{1}{1.224}\times494.22$$

$$= 403.77\text{ m/s}$$

Illustration - 15 *Two gases A and B have the same magnitude of most probable speed at 298 K for A and 150 K for B. Calculate the ratio of their molar masses* $\left(\frac{M_A}{M_B}\right)$.

(A) 2 : 1 **(B)** 1 : 0.75 **(C)** 1 : 2 **(D)** 3 : 1

SOLUTION : (A)

$$\text{Most probable speed} = \left(\frac{2RT}{M}\right)^{1/2}$$

$$\text{According to the problem } \frac{T_A}{M_A} = \frac{T_B}{M_B}$$

$$\therefore \quad \frac{M_A}{M_B} = \frac{T_A}{T_B} = \frac{298}{150} \approx 2$$

$$\therefore \quad M_A : M_B = 2 : 1$$

Illustration - 16 *What is the ratio of kinetic energy per mole of Argon at* 27°C and Helium at 127°C ?

(A) 0.75 : 1 **(B)** 1 : 1 **(C)** 1 : 0.67 **(D)** 1 : 1.25

SOLUTION : (A)

$$\text{Kinetic energy (KE)} = \frac{3}{2}RT$$

$$KE_{Ar} = \frac{3}{2}RT_{Ar}$$

$$KE_{He} = \frac{3}{2}RT_{He}$$

$$\frac{KE_{Ar}}{KE_{He}} = \frac{T_{Ar}}{T_{He}} = \frac{300}{400} = \frac{3}{4}$$

$KE_{Ar} : KE_{He}$ is 0.75 : 1