KINETIC MOLECULAR THEORY OF GASES

Maxwell and Boltzmann (1859) developed a mathematical theory to explain the behaviour of gases and the gas laws. It is based on the fundamental concept that **a gas is made of a large number of molecules in perpetual motion.** Hence the theory is called the **kinetic molecular theory** or simply the **kinetic theory of gases** (The word kinetic implies motion). The kinetic theory makes the following assumptions.

Assumptions of the Kinetic Molecular Theory

(1) **A gas consists of extremely small discrete particles called molecules dispersed throughout the container.** The actual volume of the molecules is negligible compared to the total volume of the gas. The molecules of a given gas are identical and have the same mass (*m*).

(2) **Gas molecules are in constant random motion with high velocities.** They move in straight lines with uniform velocity and change direction on collision with other molecules or the walls of the container. Pool table analogy is shown in Fig.10.17.

(3) The distance between the molecules are very large and it is assumed that van der Waals attractive forces between them do not exist. Thus **the gas molecules can move freely, independent of each other.**

(4) All collisions are perfectly elastic. Hence, **there is no loss of the kinetic energy of a molecule during a collision.**

(5) **The pressure of a gas is caused by the hits recorded by molecules on the walls of the container.**

(6) The average kinetic energy $\left(\frac{1}{2}mv^2\right)$ of the gas molecules is directly proportional to absolute temperature (Kelvin temperature). This implies that **the average kinetic energy of molecules is the same at a given temperature.**

How Does an Ideal Gas Differ from Real Gases ?

A gas that confirms to the assumptions of the kinetic theory of gases is called an ideal gas. It obeys the basic laws strictly under all conditions of temperature and pressure.

The **real gases** as hydrogen, oxygen, nitrogen etc., are opposed to the assumptions (1), (2) and (3) stated above. Thus :

(*a*) The actual volume of molecules in an ideal gas is negligible, while in a real gas it is appreciable.

(*b*) There are no attractive forces between molecules in an ideal gas while these exist in a real gas.

(*c*) Molecular collisions in an ideal gas are perfectly elastic while it is not so in a real gas.

For the reasons listed above, real gases obey the gas laws under moderate conditions of temperature and pressure. At very low temperature and very high pressure, the clauses (1), (2) and (3) of kinetic theory do not hold. Therefore, under these conditions the real gases show considerable deviations from the ideal gas behaviour.

DERIVATION OF KINETIC GAS EQUATION

Starting from the postulates of the kinetic molecular theory of gases we can develop an important equation. This equation expresses PV of a gas in terms of the number of molecules, molecular mass and molecular velocity. This equation which we shall name as the *Kinetic Gas Equation* may be derived by the following clauses.

Let us consider a certain mass of gas enclosed in a cubic box (Fig. 10.18) at a fixed temperature. Suppose that :

the length of each side of the box	$= l$ cm
the total number of gas molecules	$= n$
the mass of one molecule	$= m$
the velocity of a molecule	$= v$

The kinetic gas equation may be derived by the following steps :

(1) Resolution of Velocity v of a Single Molecule Along X, Y and Z Axes

According to the kinetic theory, a molecule of a gas can move with velocity v in any direction. Velocity is a vector quantity and can be resolved into the components v_x, v_y, v_z along the X, Y and Z axes. These components are related to the velocity v by the following expression.

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Now we can consider the motion of a single molecule moving with the component velocities independently in each direction.

(2) The Number of Collisions Per Second on Face A Due to One Molecule

Consider a molecule moving in OX direction between opposite faces A and B. It will strike the face A with velocity v_x and rebound with velocity $-v_x$. To hit the same face again, the molecule must travel l cm to collide with the opposite face B and then again l cm to return to face A. Therefore,

$$\text{the time between two collisions of face } A_v = \frac{2l}{v_x} \text{ seconds}$$

$$\text{the number of collisions per second on face } A = \frac{v_x}{2l}$$

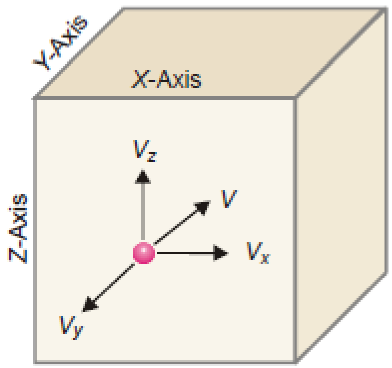

Figure 10.18
Resolution of velocity v into components V_x, V_y and V_z.

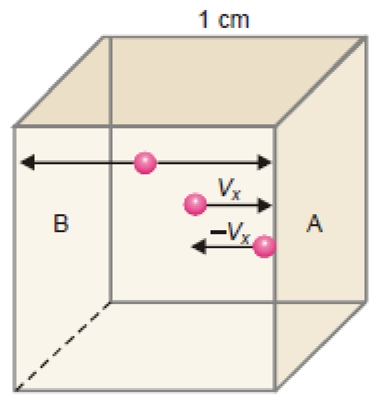

Figure 10.19
Cubic box showing molecular collisions along X axis.

(3) The Total Change of Momentum on All Faces of the Box Due to One Molecule Only

Each impact of the molecule on the face A causes a change of momentum (mass × velocity) :

	the momentum before the impact	$= mv_x$
	the momentum after the impact	$= m(-v_x)$
∴	the change of momentum	$= mv_x - (-mv_x)$
		$= 2mv_x$

But the number of collisions per second on face A due to one molecule $= \dfrac{v_x}{2l}$

Therefore, the total change of momentum per second on face A caused by one molecule

$$= 2m\, v_x \times \left(\frac{v_x}{2l}\right) = \frac{m\, v_x^2}{l}$$

The change of momentum on both the opposite faces A and B along X-axis would be double *i.e.*, $2mv_x^2/l$ similarly, the change of momentum along Y-axis and Z-axis will be $2mv_y^2/l$ and $2mv_z^2/l$ respectively. Hence, the overall change of momentum per second on all faces of the box will be

$$= \frac{2mv_x^2}{l} + \frac{2mv_y^2}{l} + \frac{2mv_z^2}{l}$$

$$= \frac{2m}{l}(v_x^2 + v_y^2 + v_z^2)$$

$$= \frac{2m\, v^2}{l} \qquad (\quad v^2 = v_x^2 + v_y^2 + v_z^2)$$

(4) Total Change of Momentum Due to Impacts of All the Molecules on All Faces of the Box

Suppose there are N molecules in the box each of which is moving with a different velocity v_1, v_2, v_3, etc. The total change of momentum due to impacts of all the molecules on all faces of the box

$$= \frac{2m}{l}(v_1^2 + v_2^2 + v_3^2 + ...)$$

Multiplying and dividing by n, we have

$$= \frac{2mN}{l}\left(\frac{v_1^2 + v_2^2 + v_3^2 + ...}{n}\right)$$

$$= \frac{2mN\, u^2}{l}$$

where u^2 is the **mean square velocity.**

(5) Calculation of Pressure from Change of Momentum; Derivation of Kinetic Gas Equation

Since force may be defined as the change in momentum per second, we can write

$$\text{Force} = \frac{2mN\,u^2}{l}$$

But
$$\text{Pressure} = \frac{\text{Total Force}}{\text{Total Area}}$$

$$P = \frac{2mNu^2}{l} \times \frac{1}{6l^2} = \frac{1}{3}\frac{mNu^2}{l^3}$$

Since l^3 is the volume of the cube, V, we have

$$P = \frac{1}{3}\frac{mNu^2}{V}$$

or
$$P\,V = \frac{1}{3}\,mNu^2$$

This is the fundamental equation of the kinetic molecular theory of gases. It is called the **Kinetic Gas equation.** This equation although derived for a cubical vessel, is equally valid for a vessel of any shape. The available volume in the vessel could well be considered as made up of a large number of infinitesimally small cubes for each of which the equation holds.

Significance of the term *u*. As stated in clause (4) u^2 is the mean of the squares of the individual velocities of all the N molecules of the gas. But $u = \sqrt{u^2}$. Therefore u is called the **Root Mean Square (or RMS) Velocity.**

KINETIC GAS EQUATION IN TERMS OF KINETIC ENERGY

If N be the number of molecules in a given mass of gas,

$$P\,V = \frac{1}{3}\,mNu^2 \qquad \text{(Kinetic Gas equation)}$$

$$= \frac{2}{3}N \times \frac{1}{2}mu^2$$

$$= \frac{2}{3}N \times e$$

where e is the average kinetic energy of a single molecule.

$$\therefore \qquad PV = \frac{2}{3}Ne = \frac{2}{3}E$$

or $$PV = \frac{2}{3}E \qquad ...(1)$$

where E is the total kinetic energy of all the N molecules. The expression (1) may be called the kinetic gas equation in terms of kinetic energy.

We know that the General ideal gas equation is

$$PV = nRT \qquad ...(2)$$

From (1) and (2)

$$\frac{2}{3}E = nRT \qquad ...(3)$$

For one mole of gas, the kinetic energy of N molecules is,

$$E = \frac{3RT}{2} \qquad ...(4)$$

Since the number of gas molecules in one mole of gas in N_0 (Avogadro number),

$$e = \frac{E}{N_0} = \frac{3RT}{2N_0}$$

or $$e = \frac{3RT}{2N_0} \qquad ...(5)$$

substituting the values of R, T, N_0, in the equation (5), the average kinetic energy of a gas molecule can be calculated.