# Kinetic Theory of Gases:

Assumptions of the kinetic theory of gases:

In developing the kinetic theory of gases, following are the simplified examples that have been made:

(i) A gas consists of a large number of identical molecules which are minute hard elastic spheres which are moving randomly in all possible directions with different velocities.

(ii) During the motion, molecules collide with one another and also with the walls of the container. The collisions are perfectly elastic, i.e., there is no loss of kinetic energy when the collisions occur. The chance of collision is same in all directions and collisions do not affect the density of molecules.

(iii) The molecules exert no forces on each other except when they actually collide. Therefore, between two successive collisions molecules move in straight lines with uniform velocity.

(iv) The collisions are instantaneous, i.e. the duration of collision is negligible compared to the time between collisions.

(vi) Since the molecules are like geometrical point masses, the actual volume occupied by them is negligible compared to the total volume of the gas (i.e. the container).

Deduction of the perfect gas equation:

Calculation of pressure
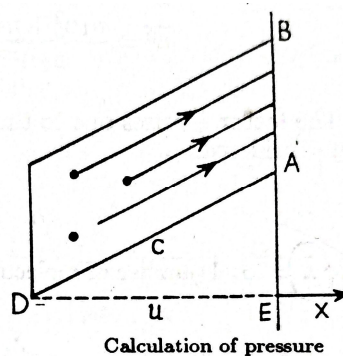
Let us consider a perfect gas enclosed in a container such that one of its surface is perpendicular to the X-axis. In the figure, BAE represents the surface.

Let c be the velocity of a molecule which has three components u, v and w along the three rectangular coordinates X, Y and Z such that

$$c^2 = u^2 + v^2 + w^2 \quad \text{.................................(1)}$$

Now, due to collision with the wall DAE, the X-component of velocity which is u, suffers change in direction where the other two components v, w remain unchanged. The change in momentum of a molecule is

$$mu - (-mu) = 2mu$$

If n_u be the number of molecules per unit volume moving with velocity u, the number of molecules which will strike unit area of the wall in time dt would be contained in a cylinder of area unity and height udt.

Number of such molecules in the cylinder = $n_u(udt)$

Total change in momentum per unit area suffered by all such molecules in time dt =

$$n_u udt.2mu = 2mn_u u^2 dt$$

Therefore, the above quantity for all the molecules moving in the positive X-direction, i.e., total change in momentum per unit area in time dt is $2m\sum_0^\infty n_u u^2 dt$.

If the above change in momentum results in force $\delta\vec{F}$, then

$$\delta\vec{F}.dt = 2m\sum_0^\infty n_u u^2 dt$$

$$\therefore \delta\vec{F} = 2m\sum_0^\infty n_u u^2$$

Since the area involved here is unity, $\delta\vec{F}$ is the pressure p_x.

$$\therefore p_x = 2m\sum_0^\infty n_u u^2 \quad ....(2)$$

Where n_u is a function of u.

If $\overline{u^2}$ be the mean square velocity, we can write

$$\overline{u^2} = \frac{n_1 u_1^2 + n_2 u_2^2 + ... + n_i u_i^2 + ...}{n_1 + n_2 + ... + n_i + ...} = \frac{\sum n_i u_i^2}{\sum n_i} = \frac{\sum n_i u_i^2}{n/2}$$

Where n is the number of molecules per unit volume.

The factor $\dfrac{1}{2}$ arises due to the fact that molecules only moving in the positive X-direction are being considered.

$$\therefore \sum_0^\infty n_u u^2 = \frac{n}{2}\overline{u^2}$$

$$\therefore p_x = 2m.\frac{n}{2}\overline{u^2} = mn\overline{u^2}$$

Similarly, $p_y = mn\overline{v^2}$ and $p_z = mn\overline{w^2}$.

Therefore, the expression for the pressure is

$$p = p_x = p_y = p_z = mn\overline{u^2} = mn\overline{v^2} = mn\overline{w^2}$$

But $\overline{u^2} = \overline{v^2} = \overline{w^2} = \dfrac{1}{3}\overline{c^2}$, where $\overline{c^2}$ is the mean square velocity.

$$\therefore p = \frac{1}{3}mn\overline{c^2} = \frac{1}{3}mnC^2,$$

where $C = \sqrt{\overline{c^2}}$ is the root mean square or r.m.s. velocity.

The expression for pressure can also be written as

$$p = \frac{1}{3}\rho C^2$$

where $\rho = mn$ is the density of the gas.

Deductions from pressure expression:

(i) R.M.S velocity:

Pressure p is given by

$$p = \frac{1}{3}\rho C^2$$

$$\therefore C = \sqrt{\frac{3p}{\rho}}$$

This gives the expression of r.m.s velocity of the gas. It should be noted that lighter the gas, faster would be its motion.

Let us consider a gramme-mole of the gas. If M be the molecular weight and V be the volume of 1 gm-mole of the gas, then

$$\rho = \frac{M}{V}$$

$$\therefore p = \frac{1}{3}\rho C^2 = \frac{1}{3}\frac{M}{V}C^2$$

$$\therefore pV = \frac{1}{3}MC^2$$

For 1 gm-mole of the gas, we have $pV = RT$. Therefore,

$$\frac{1}{3}MC^2 = RT$$

$$\therefore C = \sqrt{\frac{3RT}{M}}$$

This is an alternate expression for the r.m.s velocity of the gas. From this expression we can see that

The r.m.s velocity is proportional to the square root of temperature the gas, i.e., $C \propto \sqrt{T}$.

(ii) Pressure and kinetic energy:

We have,

$$p = \frac{1}{3}\rho C^2 = \frac{2}{3}\cdot\frac{1}{2}\rho C^2 = \frac{2}{3}E$$

where $E = \frac{1}{2}\rho C^2$ is the kinetic energy of the gas molecules per unit volume.

Thus, the pressure of a gas is equal to two-thirds of the mean kinetic energy of translation of the gas molecules per unit volume.

This is one of the most important conclusions of the kinetic theory of an ideal gas. The above equation gives a relationship between molecular quantities, i.e, quantities relating to an individual molecule, and the pressure of the gas which is a macroscopic quantity which can be directly measured. It is sometimes called the fundamental equation of the kinetic theory.

(iii) Boyle's law:

The pressure of a gas is given by

$$p = \frac{1}{3}\rho C^2$$

If M be the mass of a gas that occupies a volume V at temperature T, then density, $\rho = \frac{M}{V}$.

$$\therefore p = \frac{1}{3}\frac{M}{V}C^2$$

$$\therefore pV = \frac{1}{3}MC^2$$

At constant temperature r.m.s velocity C is a constant. Hence, at constant temperature $pV =$ constant. This is Boyle'slaw.

(iv) Gay-Lussac law (Charles' law):

We know that $pV = \frac{1}{3}MC^2$.

$\therefore pV \propto C^2$

Again, $C^2 \propto T$

Therefore, $pV \propto T$

Or, $\frac{V}{T} = $ constant at constant pressure.

This is Gay-Lussac law or Charles' law.

(v) Dalton's law of partial pressures:

Let $m_1, m_2, m_3, \ldots\ldots$ be the molecular masses of different gases $1, 2, 3, \ldots\ldots$ and $n_1, n_2, n_3, \ldots\ldots$ be their respective number of molecules per unit volume. If we assume no interaction between gas molecules, at equilibrium the total pressure will be due to all the different types of molecules.

$\therefore p = \frac{1}{3}m_1 n_1 C_1^2 + \frac{1}{3}m_2 n_2 C_2^2 + \frac{1}{3}m_3 n_3 C_2^2 + \ldots\ldots$

But, $\frac{1}{3}m_1 n_1 C_1^2 = p_1 = $ partial pressure of gas 1

$\frac{1}{3}m_2 n_2 C_2^2 = p_2 = $ partial pressure of gas 2 and so on.

$\therefore p = p_1 + p_2 + p_3 + \ldots\ldots = \sum_i p_i$

Thus, the pressure of a mixture of gases is equal to the sum of partial pressures of its component gases. This is Dalton's law of partial pressures.

(vi) Avogadro's hypothesis:

Let us consider two different gases contained in two different enclosures, each of volume V. Let m_1, N_1, C_1 be the molecular mass, number of molecules per unit volume and r.m.s velocity respectively of gas1; let m_2, N_2, C_2 be the corresponding quantities for gas 2.

When the pressure is same for both the gases, we have

$\frac{1}{3}m_1 \frac{N_1}{V}C_1^2 = \frac{1}{3}m_2 \frac{N_2}{V}C_2^2$

Or, $\dfrac{1}{3}m_1 N_1 C_1^2 = \dfrac{1}{3}m_2 N_2 C_2^2$ ....(1)

When the temperature is the same, we have

$\dfrac{1}{2}m_1 C_1^2 = \dfrac{1}{2}m_2 C_2^2$ ....(2)

Dividing eq. (1) by eq. (2), we have

$N_1 = N_2$

Thus, for the same temperature and pressure, equal volumes of all gases contain equal number of molecules. This is Avogadro's hypothesis.

(vii) Graham's law of diffusion:

Let two vessels of equal volume contain two gases 1 and 2, at the same temperature and pressure. According to Avogadro's hypothesis, each gas have the same number of molecules. Since the number of molecules is the same, the number of molecules n_1 and n_2 which diffuse (provided the diffusion is allowed) will be in the ration of their speeds, which again will be in the same ratio as r.m.s speeds.

$\therefore \ \dfrac{n_1}{n_2} = \dfrac{C_1}{C_2}$ ....(a)

Since the pressures are also the same, we may write

$\dfrac{1}{3}\rho_1 C_1^2 = \dfrac{1}{3}\rho_2 C_2^2$

Or, $\dfrac{C_1}{C_2} = \sqrt{\dfrac{\rho_2}{\rho_1}}$ ....(b)

From equations (a) and (b) we have,

$\dfrac{n_1}{n_2} = \sqrt{\dfrac{\rho_2}{\rho_1}}$

This is Graham's law of diffusion.

(viii) Clapeyron's equation:

The pressure p is given by

$p = \dfrac{1}{3}mnC^2 = \dfrac{1}{3}\dfrac{M}{N_A}nC^2$,

where M is the molecular weight of the gas and N_A is the Avogadro's number.

$$\therefore p = \frac{1}{3}\frac{n}{N_A}MC^2 = \frac{n}{N_A}X\frac{1}{3}MC^2 = \frac{n}{N_A}pV \qquad [\because pV = \frac{1}{3}MC^2]$$

$$\therefore p = \frac{n}{N_A}RT = n\frac{R}{N_A}T = nkT \qquad [\because k = \frac{R}{N_A} = \text{Boltzmann constant}]$$

$$\therefore p = nkT$$

This is Clapeyron's equation.

Using the result of the kinetic theory of gases, we thus obtain the laws controlling the behaviours of gases that were established long before the theory was developed. To a certain extent this confirms the truth of the theory.

Introduction of temperature:

To introduce the temperature in kinetic theory of gases, we recall the equation

$$C^2 = \frac{3RT}{M} \quad \text{...............(1)}$$

We see that C^2 is proportional to the absolute temperature. But mean kinetic energy of translation is proportional to C^2. Thus we may accordingly consider that the mean kinetic energy of translation manifests itself as the temperature of the gas. This is the kinetic interpretation of temperature.

At $T = 0$, $C = 0$ which means that, according to the kinetic theory, the absolute zero is the temperature at which all molecular motions cease. However, this conclusion is not justified as the perfect gas state itself does not hold up to absolute zero of temperature. Further, quantum theory predicts the existence of some energy at absolute zero, called the 'zero-point' energy.

From eq. (1), we may write

$$\frac{1}{2}MC^2 = \frac{3}{2}RT$$

Dividing both sides by N_A, the Avogadro's number

$$\frac{1}{2}\frac{M}{N_A}C^2 = \frac{3}{2}\frac{R}{N_A}T$$

Or, $\frac{1}{2}mC^2 = \frac{3}{2}kT$ ....(2)

Here m is the molecular mass and k is the Boltzmann constant.

Eq. (2) shows that the mean kinetic energy of translation per molecule is $\frac{3}{2}kT$ and is proportional to the absolute temperature. So corresponding to a temperature, there is a kinetic energy and molecular collisions lead to a uniform temperature (thermal equilibrium).

Various constants involved in kinetic theory:

(i) Avogadro number (N_A):

If m be the molecular mass and M be the molecular weight, then

$$N_A = \frac{M}{m} = \frac{2\,gm}{3.32\,X10^{-24}\,gm}, \text{ here we have taken H}_2 \text{ gas}$$

$$\therefore N_A = 6.023\,X10^{23} / gm - mole$$

(ii) Universal gas constant (R):

We know, $pV = RT$ for one mole of a gas.

$$R = \frac{pV}{T} = \frac{(76\,X13.6\,X981)\,X(22.4\,X10^3)}{273}\,\text{erg / mole / K}$$
$$= 8.31\,X10^7\,\text{erg / mole / K} = 8.31\,\text{Joule / mole / K}$$
$$= \frac{8.31\,X10^7}{4.18\,X10^7}\,Cal / \text{mole / K} = = 1.99\,\text{Cal/ mole/ K}$$
$$= \frac{1\,X22.4}{273}\,\text{lit- atmos/ mole/ K} = 0.082\,\text{lit- atmos/ mole/ K}$$

(iii) Boltzmann constant (k):

$$k = \frac{R}{N_A} = \frac{8.31\,X10^7\,\text{erg / mole / K}}{6.023\,X10^{23} / \text{mole}} = 1.38\,X10^{-16}\,\text{erg/ K} = 1.38\,X10^{-23}\,\text{J/ K}$$