Kinetic Theory of Gases

Gas Molecule

Container

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Ideal gas equation

Many of the properties of gases are common at low pressures and high temperatures. The pressure, volume and the temperature (in kelvin) of such a gas obey the equation.

pV = nRT

where n is the amount of gas in number of moles and R is universal gas constant having a value 8.314 J/mol-K. The above equation is called ideal gas equation and a gas obeying this equation is called ideal gas.

Kinetic theory of gases

Any sample of a gas is made of molecules which is the smallest unit having all the chemical properties of the sample. The detailed behaviour of large number of molecules of gas results in its observed behaviour. The properties of a gas may be investigated from the point of view of kinetic theory based on the laws of classical mechanics.

Postulates of kinetic theory gases

a. All gases are made up of identical particles called molecules.

b. The size of a molecule is much smaller than the average separation between the molecules.

c. The molecules of a gas are in a state of continuous random motion in all the directions.

d. The molecules collide with each other and also with the walls of the container. The molecules travel in straight line between collisions.

e. The collisions are perfectly elastic and time spent during collisions is very small compared to the time of their random motion.

f. The molecules exert no force on each other or on the walls of the container except during collisions.

g. The molecules obey Newton's laws of motion.

The expression for the pressure of an ideal gas

During the collisions, the molecules exert forces on the walls of the container. This is the origin of the pressure of a gas. Based on kinetic theory of gases it can be shown that

$$pV = \frac{1}{3}Nm(v^2)_{avg} \qquad \cdots (1)$$

where   p = pressure of the gas

V = volume of the gas

N = total number of molecules in the sample

m = mass of a single molecule

$(v^2)_{avg}$ = average of the speeds squared of the molecules. It is also called mean square speed.

Equation (1) can be written as

$$pV = \frac{2}{3}N\left[\frac{1}{2}m(v^2)_{avg}\right] \qquad \cdots (2)$$

$\frac{1}{2}m(v^2)_{avg}$ gives average translational kinetic energy of single molecule. $N\left[\frac{1}{2}m(v^2)_{avg}\right]$ gives total translational kinetic energy of all the molecules due to random motion. It is denoted by K_{tr}.

$$\therefore \ pV = \frac{2}{3}K_{tr} \qquad \cdots (3)$$

From ideal gas equation

$$pV = nRT \qquad \cdots (4)$$

Comparing (3) and (4)

$$K_{tr} = \frac{3}{2}nRT = \frac{3}{2}pV \qquad \cdots (5)$$

Thus, average translational kinetic energy of molecules of a gas is proportional to its absolute temperature.

Average kinetic energy per mole is given by

$$\frac{K_{tr}}{n} = \frac{3}{2}RT = \frac{1}{2}M(v^2)_{avg} \qquad \dots (6)$$

where M = molecular weight

The average translational kinetic energy of a molecule is given by

$$\frac{1}{2}m(v^2)_{avg} = \frac{3nRT}{2N}$$

Since $R = N_A K$; $nN_A = N$

$$\frac{1}{2}m(v^2)_{avg} = \frac{3}{2}kT \qquad \dots (7)$$

RMS speed

The square root of the mean square speed is called root mean square speed and is denoted by v_{rms}.

$$\therefore \ v_{rms} = \sqrt{(v^2)_{avg}}$$

Thus average translational kinetic energy of a molecule is given by

$$\frac{1}{2}mv_{rms}^2 = \frac{3}{2}kT \quad \text{or} \quad v_{rms} = \sqrt{\frac{3kT}{m}} \quad \dots (8)$$

The average translational kinetic energy per mole given by

$$\frac{1}{2}Mv_{rms}^2 = \frac{3}{2}RT$$

$$\therefore \ v_{rms} = \sqrt{\frac{3RT}{M}} \qquad \dots (9)$$

The average speed v_{avg} is some what smaller than the rms speed. It can be shown that

$$v_{avg} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \qquad \dots (10)$$

where M = Molecular weight

Most probable speed

It is defined as the speed which is possessed by maximum fraction of total number of molecules of the gas. It is given by

$$v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

☞ When mixture of two gases A and B are in thermal equilibrium, the average kinetic energy of all molecules are equal. If v_1 and v_2 be the rms speeds of the molecules A and B respectively,

$$\frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2 \qquad \dots (11)$$

∴ Thus, the heavier molecules move with smaller rms speed and the lighter molecules move with larger rms speed.

Mean free path

Mean free path is the average distance travelled by a molecule between collisions. It is given by

$$\lambda = \frac{1}{\dfrac{\sqrt{2}\pi d^2 N}{V}} = \frac{1}{\sqrt{2}\pi d^2 n_V}$$

where d is the diameter of each molecule and $n_V = \dfrac{N}{V}$ is the number of molecules per unit volume.

Collision frequency

The number of collisions per unit time is called the collision frequency. It is given by

$$f = \frac{\overline{v}}{\lambda} = \sqrt{2}\pi d^2 \overline{v} n_v$$

where $\overline{v}$ = average speed of the molecules.

The average time between successive collisions is given by

$$t = \frac{1}{f} = \frac{\lambda}{v} = \frac{1}{\sqrt{2}\pi d^2 \overline{v} n_V}$$

☞ The number of collisions made by gas molecules on unit area of the wall per unit time is given by $f = \frac{1}{4} n_V \overline{v}$

Degrees of freedom

Degrees of freedom of a gas molecule determine the minimum number of independent velocity components needed to describe the motion of that molecule.

For a monatomic gas molecule there are three degrees of freedom (for the velocity components v_x, v_y, v_z).

For a diatomic molecule, in addition to the three degrees of freedom (due to translation), there are two more degrees of freedom due to rotation. There are two possible axes of rotation perpendicular to each other and to the molecules axis. Thus, there are 5 degrees of freedom for a diatomic molecule.

(Vibrational motion can also contribute to the degrees of freedom. But a change in the temperature does not cause change in their average vibrational energy appreciably and hence the vibrational degrees of freedom are said to be frozen out).

When the vibrational degrees of freedom are also taken into account, the degrees of freedom are

6 n – 6   for non-linear molecules

6 n – 5   for linear molecules, where n = number of atoms in a molecule.

For a polyatomic molecule, the degrees of freedom depend on the actual arrangement of atoms in the molecules.

☞ Degrees of freedom can also be interpreted as the number of independent ways in which a molecule can store energy.

Law of equipartition of energy

Law of equipartition of energy states that the average energy of a molecule in a gas associated with each degree of freedom is $\frac{1}{2}$ kT, where k is Boltzmann's constant and T is the absolute temperature.

Thus, we can write that the total energy associated with a monatomic gas molecule as $K = 3\left(\frac{1}{2}kT\right)$; that associated with a diatomic gas molecule as $K = 5\left(\frac{1}{2}kT\right)$ etc.

Specific heat of gases

Unlike solids and liquids, gases have larger coefficients of expansion. The state of gas can be changed to different states via different processes. Each process corresponds to a specific heat for the gas along the path. In principle, a gas has infinite number of specific heats. Out of those, two specific heats are practically important. They are: specific heat at constant pressure (C_p) and specific heat at constant volume (C_v) respectively.

Specific heat at constant pressure (C_p) is the amount of heat required to raise the temperature of one mole of an ideal gas at constant pressure.

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