Semester III, Paper I: THERMAL PHYSICS

Unit I: Kinetic Theory of Gases and Transport Phenomena

1.1 Introduction:

The kinetic theory of gases attempts to explain the macroscopic properties of a gas such as their pressure, volume, temperature, density, kinetic energy in terms of temperature, etc. in terms of the motion of its molecules and the interactions which lead to macroscopic relationships like ideal gas law. The gas is assumed to consist of a large number of identical, discrete particles called molecules, a molecule being the smallest unit having the same chemical properties as the substance. Elements of kinetic theory were developed by Maxwell, Boltzmann and Clausius between 1860-1880's. Kinetic theories are available for gas, solid as well as liquid. However, we will discuss here about the kinetic theory of gases only.

1.2 Ideal Gas Equation:

The gases at low pressures and at temperature far above their condensation point obeys the following relation between their pressure (P), volume (V) and temperature (T),

$$PV = nRT \qquad \text{..............................} \quad (1)$$

Here, n - is the number of moles and R = 8.314 J/mol.K. R is called Universal Gas Constant. Gases which obey the equation (1) are called **ideal gases**.

1.3 Postulates of Kinetic Theory of Gases

The following assumptions are made in developing Kinetic theory of gases. The Kinetic theory of gases developed with these assumptions explain the macroscopic properties of the materials.

i. All gases consist of some basic units called molecules. The molecules are made up of single or group of atoms depending on the chemical nature of the gas. The molecules of same gas are alike and differ from the molecules of other gas.
ii. The size of the molecule is very small compared to the average intermolecular distance. Molecules do not exert any force among themselves or to the walls except during collision.
iii. The molecules move in random direction with random speed.
iv. The molecules undergo collisions among themselves and to the walls of the container. These collisions are perfectly elastic. The collision time is very small compared to the average time spent by a molecule between two collisions.
v. The molecules obey Newton's Law of Motion.
vi. The number of gas molecules is so large that at every position of infinitesimal volume of the container, the density and distribution of different physical parameters are same. The above parameters are also independent of direction and time at a steady state.

1.4 Pressure Exerted by Gas:

The molecules of a gas are in a state of random motion. When a certain mass of a perfect gas is enclosed inside a container, molecules continuously collide against the walls of the container. During each collision, momentum is transferred to the walls of the container.

The pressure exerted by the gas is due to the continuous collision of the molecules against the walls of the container. Due to this continuous collision, the walls experience a continuous force which is equal to the total momentum imparted to the walls per second. The force experienced per unit area of the walls of the container determines the pressure exerted by the gas.

Consider a perfect gas enclosed in a container. Let m be the mass of each molecule and n number of molecules present in container of volume V. Therefore, $M = mn$ where M is the mass of the gas of volume V. Then, the pressure exerted by the gas (P) on the walls of the container is given by,

$$P = \frac{1}{3}\frac{mn}{V}\bar{c}^2 = \frac{1}{3}\frac{M\,\bar{c}^2}{V}$$

Where, $\bar{c}$ is called the root mean square (RMS) velocity, which is defined as the square root of the mean value of the squares of velocities of individual molecules.

1.5 Derivation of Maxwell's Law of Distribution of Velocities and its Experimental Verification:

It was shown that the rms velocity of the molecules of gas is related to the gas temperature. If all the molecules of a gas at a certain temperature move at the same speed, then the rms value indicates the magnitude of the velocity of all the molecules. However, the speeds of gas molecules vary widely, and it is thus necessary to determine the velocity distribution of the molecule, so that the number of molecules moving with any particular velocity can be determined.

In 1852, James Clerk Maxwell found an equation for the velocity distribution of gas molecules, which is known as Maxwell's velocity distribution law.

The molecules of an ideal gas possesses average kinetic energy which is given by,

$$\bar{E}_k = \frac{1}{2}m.\bar{c}^2 \qquad \text{........ (i)}$$

Where, m is mass of the molecule and $\bar{c}$ is average velocity of the molecule.

Pressure exerted by an ideal gas is given by,

$$P = \frac{1}{3}\frac{M\,\bar{c}^2}{V} = \frac{1}{3}\rho.\bar{c}^2 \qquad \text{...... (ii)}$$

The equation of state for ideal gas is given by,

$$PV = RT \qquad \text{...... (iii)}$$

Combining equation (ii) and (iii) we get expression for average velocity as,

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

$$= \left(\frac{3kT}{m}\right)^{1/2}$$

1.6 Degree of Freedom:

The Degree of Freedom (DOF) of a body is defined as the total number of independent variables or co-ordinates that determine the state of a physical system.

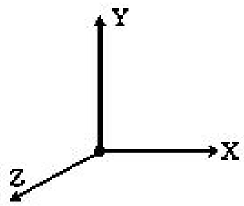
For translatory motion

(a) A particle moving in a straight line along any one of the axes has one degree of freedom (e.g.) an ant moving along a straight line.

(b) A particle moving in a plane (X and Y axes) has two degrees of freedom. (e.g.) an ant that moves on a floor.

(c) A particle moving in space (X, Y and Z axes) has three degrees of freedom. (e.g.) a bird that flies.

A rigid body with finite mass has both rotatory and translatory motion. The rotatory motion also can have three co-ordinates in space, like translatory motion; therefore a rigid body will have six degrees of freedom; three due to translatory motion and three due to rotatory motion.

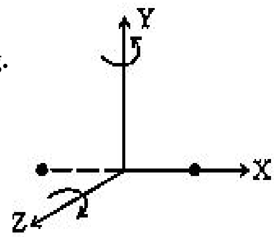


Monoatomic molecule

Since a monoatomic molecule consists of only a single atom of point mass it has three degrees of freedom of translatory motion along the three co-ordinate axes as shown in figure.
Examples: molecules of rare gases like helium, argon, etc.

Fig. le

Diatomic molecule



The diatomic molecule can rotate about any axis at right angles to its own axis. Hence it has two degrees of freedom of rotational motion in addition to three degrees of freedom of translational motion along the three axes. So, a diatomic molecule has five degrees of freedom as shown in figure. Examples: molecules of O_2, N_2, CO, Cl_2, etc.

Triatomic molecule (Linear type)

In the case of triatomic molecule of linear type, the centre of mass lies at the central atom. It, therefore, behaves like a diatomic molecule with three degrees of freedom of translation and two degrees of freedom of rotation, totally it has five degrees of freedom as shown in figure. Examples molecules of CO_2, CS_2, etc.

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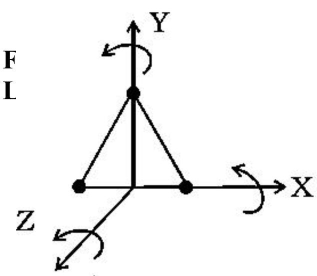
Triatomic molecule (Non-linear type)



A triatomic non-linear molecule may rotate, about the three mutually perpendicular axes, as shown in figure. Therefore, it possesses three degrees of freedom of rotation in addition to three degrees of freedom of translation along the three co-ordinate axes Hence it has six degrees of freedom Examples : molecules of H_2O, SO_2, etc.

Fig. 1.4 Triatomic Molecule Non-linear

In above cases, only the translatory and rotatory motion of the molecules is considered. The vibratory motion of the molecules can take into consideration at high temperature.

1.7 Law of Equipartition of Energy:

In 1859, James Clerk Maxwell argued that the kinetic heat energy of a gas is equally divided between linear and rotational energy. In 1876, Ludwig Boltzmann expanded on this principle by showing that the average energy was divided equally among all the independent components of motion in a system.

Law of equipartition of energy states that for a dynamical system in thermal equilibrium the total energy of the system is equally divided among all the degrees of freedom. The energy associated with each degree of freedom per molecule is ½ kT. Where *k* is the Boltzmann's constant.

For example, an atom of a gas has three degrees of freedom (the three spatial, or position, coordinates of the atom) and will, therefore, have an average total energy of $\frac{3}{2} kT$.

Let us consider one mole of a monoatomic gas in thermal equilibrium at temperature T. Each molecule has 3 degrees of freedom due to translatory motion. According to kinetic theory of gases, the mean kinetic energy of a molecule is $\frac{3}{2} kT$.

$$\frac{1}{2} mC^2 = \frac{1}{2} mC_x^2 + \frac{1}{2} mC_y^2 + \frac{1}{2} mC_z^2$$

So, $$\frac{1}{2} mC_x^2 + \frac{1}{2} mC_y^2 + \frac{1}{2} mC_z^2 = \frac{3}{2} kT.$$

Since molecules move at random, the average kinetic energy corresponding to each degree of freedom is the same.

$$\frac{1}{2} mC_x^2 = \frac{1}{2} mC_y^2 = \frac{1}{2} mC_z^2$$

i.e. $$\frac{1}{2} mC_x^2 = \frac{1}{2} mC_y^2 = \frac{1}{2} mC_z^2 = \frac{1}{2} kT$$

Thus, mean kinetic energy per molecule per degree of freedom is ½ kT.

1.8 Mean Free Path:

According to kinetic theory of gases, the gas molecules can never move in a straight path without interruptions. They move in all possible direction with all possible velocities and collide with each other. Between every two consecutive collisions, a gas molecule travels a straight path with constant speed. The average distance of all the paths of a molecule is the mean free path.

The mean free path is the average distance travelled by a moving gas molecule between successive collisions. It is denoted by λ.

Pressure, temperature, and other factors that affect density can indirectly affect mean free path.

1.9 Sphere of Influence:

As per kinetic theory of gases, all the gas molecules are identical and perfectly elastic spheres. They move randomly in all possible direction and frequently collide with each other. We assume that the molecule A is in motion and all other molecules are at rest. Suppose, σ is the diameter of each molecule.