B.Sc. II Semester
Thermal Physics
Unit 3 - Kinetic Theory of Gases

Kinetic Theory of Gases

The kinetic theory of gases is the study that relates the microscopic properties of gas molecules (like speed, momentum, kinetic energies etc.) with the macroscopic properties of gas molecules (like pressure, temperature and volume).

Fundamental Postulates of Kinetic Theory

1. The molecules of a gas are considered to be rigid, identical in all respects. Their size is negligible compared to intermolecular distances.
2. The molecules are in random motion in all directions with all possible velocities.
3. The molecules collide with each other and with the walls of the container. The collision of molecules is perfectly elastic.
4. At each collision, velocity changes but the molecular density is constant in steady state.
5. As the collisions are perfectly elastic, there is no force of attraction or repulsion between the molecules. Thus the energy is only kinetic.
6. Between any two successive collisions, molecules travel with uniform velocity along a straight line.

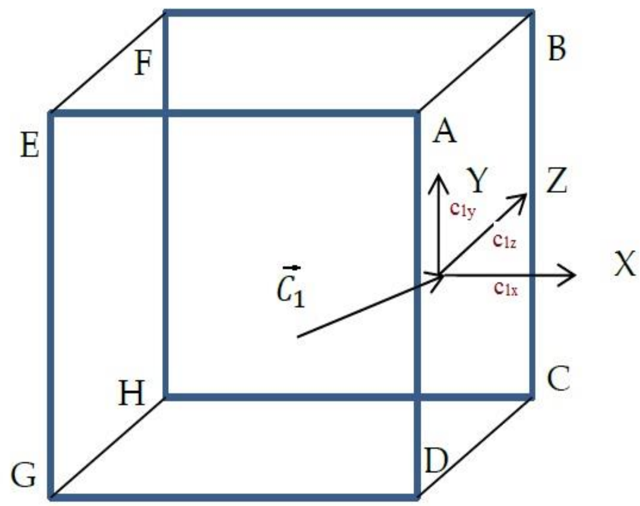
Expression for the Pressure of the Gas

Let us consider a cubical vessel of length 'L' containing 'n' number of gas molecule. Each of mass 'μ'. let $\vec{c}_1$, $\vec{c}_2$, ……$\vec{c}_n$ be the velocity of gas molecules.

The velocity $\vec{c}_1$ of first molecule can be resolved into three components c_{1x}, c_{1y} and c_{1z} along X, Y and Z directions as shown in the figure, then

$$c_1^2 = c_{1x}^2 + c_{1y}^2 + c_{1z}^2 \qquad (1)$$

The momentum of this molecule when strikes the wall ABCD (along X-Axis, parallel to YZ plane) of the vessel is equal to μc_{1x}.



Since the collision is elastic, the molecule rebounds with the same velocity; its y and z components of velocity do not change in the collision but the x-component reverses sign. That is, the X component of velocity after collision is $-c_{1x}$. The change in momentum of the molecule is

final momentum-initial momentum i.e.

$-\mu c_{1x} - \mu c_{1x} = -2\mu c_{1x}$.

By the principle of conservation of momentum, the momentum imparted to the wall in the collision = $2\mu c_{1x}$.

It strikes the wall EFHG and returns back to ABCD after travelling a distance 2L. The time between the successive collisions on ABCD is $\frac{2L}{c_{1x}}$.

The force exerted by this molecule on the wall ABCD is found using Newton's second law of motion:

$$\text{Force=Rate of Change of Momentum}=\frac{2\mu c_{1x}}{2L/c_{1x}}=\frac{\mu c_{1x}^2}{L}$$

Similarly the force exerted by by another molecule of velocity $\vec{c}_2$ having components c_{2x}, c_{2y} and c_{2z} on the wall ABCD is $\frac{\mu c_{2x}^2}{L}$.

Hence the total force F_x on the face ABCD due to all the n molecules in X-direction is given by

$$F_x = \frac{\mu}{L}\left(c_{1x}^2 + c_{2x}^2 + \dots\dots. + c_{nx}^2\right) \tag{2}$$

Since pressure is normal force per unit area, the pressure p_x on the face ABCD is given by

$$p_x = \frac{F_x}{L^2} = \frac{\mu}{L^3}\left(c_{1x}^2 + c_{2x}^2 + \dots\dots. + c_{nx}^2\right)$$

$$p_x = \frac{F_x}{L^2} = \frac{\mu}{V}\left(c_{1x}^2 + c_{2x}^2 + \dots\dots. + c_{nx}^2\right) \tag{3}$$

Where L^3=V is the volume of the cubical vessel.

Similarly if p_y and p_z are the pressure on the faces AEFB and ADGE, then

$$p_y = \frac{F_y}{L^2} = \frac{\mu}{V}\left(c_{1y}^2 + c_{2y}^2 + \dots\dots. + c_{ny}^2\right) \tag{4}$$

$$p_z = \frac{F_z}{L^2} = \frac{\mu}{V}\left(c_{1z}^2 + c_{2z}^2 + \dots\dots. + c_{nz}^2\right) \tag{5}$$

Since molecular density is uniform throughout the gas, the pressure of the gas is same in all the directions.

Thus, $$p = \frac{p_x + p_y + p_z}{3} \tag{6}$$

Using Eqns. (3, 4, 5), Eqn (6) becomes

$$p = \frac{\mu}{3V}\left[\left(c_{1x}^2 + c_{2x}^2 + \dots.. + c_{nx}^2\right) + \left(c_{1y}^2 + c_{2y}^2 + \dots.. + c_{ny}^2\right) + \left(c_{1z}^2 + c_{2z}^2 + \dots.. + c_{nz}^2\right)\right]$$

$$= \frac{\mu}{3V}\left[\left(c_{1x}^2 + c_{1y}^2 + c_{1z}^2\right) + \left(c_{2x}^2 + c_{2y}^2 + c_{2z}^2\right) + \dots\dots\dots. + \left(c_{nx}^2 + c_{ny}^2 + c_{nz}^2\right)\right]$$

$$= \frac{\mu}{3V}\left[\left(c_1^2 + c_2^2 + \dots\dots. + c_n^2\right)\right]$$ (using Eqn (1) and similar for other velocities)

$$p = \frac{1}{3}\frac{\mu n}{V}\bar{c}^2 \tag{7}$$

where $\overline{c^2} = \frac{\left(c_1^2 + c_2^2 + ...+ c_n^2\right)}{n}$ is the mean square velocity (speed) of the molecules.

If M=μn=total mass of the gas, Eqn (7) can be written as

$$p = \frac{1}{3}\frac{M}{V}\overline{c^2} \tag{8}$$

which is the required expression of average pressure exerted by all gas molecules placed inside the cubical vessel. Eqn. (8) can be written as

$$p = \frac{1}{3}\rho \overline{c^2} \tag{9}$$

where $\rho = \frac{M}{V}$ is density of the gas.

1. Average Kinetic Energy

For one mole of an ideal gas

$$pV=RT \qquad \text{(i)}$$

from kinetic theory of gases (for 1 mole)

$$p = \frac{1}{3}\frac{M}{V}\overline{c^2}$$

$$pV = \frac{1}{3}M\overline{c^2} \qquad \text{(ii)}$$

Comparing (i) and (ii) we get

$$\frac{1}{3}M\overline{c^2} = RT$$

$$\frac{1}{2}M\overline{c^2} = \frac{3}{2}RT \qquad \text{(iii)}$$

Here $\frac{1}{2}M\overline{c^2}$ is the average kinetic energy of one mole i.e. average kinetic energy of one mole gas is $\frac{3}{2}RT$.

Since N_A (Avagadro number) be the number of molecules in one mole and if μ is the mass of each molecule, then mass of one mole gas M= μ N_A. Thus from (iii)

$$\frac{1}{2}\mu N_A \overline{c^2} = \frac{3}{2}RT$$

$$\frac{1}{2}\mu\overline{c^2} = \frac{3}{2}\frac{R}{N_A}T$$

$$\frac{1}{2}\mu\overline{c^2} = \frac{3}{2}kT \qquad \text{(iv)}$$

Where $k = \frac{R}{N_A}$ is Boltzman constant.

Thus average kinetic energy per molecule is $\frac{3}{2}kT$.

Note: From (iv) we see that,

$$c_{rms} = \sqrt{\overline{c^2}} = \sqrt{\frac{3kT}{\mu}}.$$

2. Boyle's Law From Kinetic Theory of Gases

From kinetic theory of gases

$$p = \frac{1}{3}\frac{M}{V}\overline{c^2}$$

or

$$pV = \frac{1}{3}M\overline{c^2} \qquad \text{(v)}$$

since $\overline{c^2} \propto T$ (from iv), if the temperature is constant **for a given mass** of a gas , we have from (v)

$$pV = \text{constant}$$

$$p \propto \frac{1}{V}$$

i.e. pressure of a given mass of gas is inversely proportional to its volume at constant temperature , which is Boyle's law.

3. Charle's Law From Kinetic Theory of Gases

From kinetic theory of gases

$$p = \frac{1}{3}\frac{M}{V}\overline{c^2}$$

or $$V = \frac{1}{3}\frac{M}{p}\overline{c^2} \qquad \text{(vi)}$$

since $\overline{c^2} \propto T$ (from iv), if the pressure is constant **for a given mass** of a gas, we have from (vi)

$$V \propto \overline{c^2}$$
$$V \propto T$$

i.e. Volume of a given mass of gas is directly proportional to its absolute temperature at constant pressure , which is Charle’s law.

4. Perfect Gas Equation From Kinetic Theory of Gases

From kinetic theory of gases

$$p = \frac{1}{3}\frac{M}{V}\overline{c^2}$$

or $$pV = \frac{1}{3}M\overline{c^2} \qquad \text{(vii)}$$

since $\overline{c^2} \propto T$ (from iv), for one mole of the gas

$$pV \propto \overline{c^2}$$
$$pV \propto T$$
$$pV = RT$$ which is gas equation for 1 mole of ideal gas.

Where R is gas Constant.