Introduction

- The constituent particles of the matter like atoms, molecules or ions are in continuous motion.

- In solids, the particles are very close and oscillate about their mean positions.

- In gases, at low density, the particles are far away from each other and perform random motion in all directions. Also, the interactions among them are negligible.

- In liquids, the particles are slightly more away than in solids and their motion is less free than in gases.

- Pressure, temperature, volume, internal energy associated with gas are known as macroscopic physical quantities which are manifested as an average combined effect of the microscopic processes.

- Macroscopic quantities like, pressure, temperature, volume can be measured while internal energy can be calculated from them. Description of a system using these quantities is known as macroscopic description.

- Macroscopic quantities and their interrelationships can be understood from the processes occurring between the constituent particles at microscopic level, e.g., pressure of a gas can be understood from the transfer of momenta to the walls of the container by the collisions of the molecules making random motion. Thus, description of the system in relation to the speed, momentum and kinetic energy of its constituent particles is known as microscopic description.

Kinetic theory of gases is an approach wherein the laws of mechanics are applied (statistically) to the constituent particles of the system (i.e., gas) and macroscopic quantities are obtained in terms of its microscopic quantities with the help of a mathematical scheme.

11.1 Laws of ideal gas

Boyle's law:

"At constant temperature, volume of a fixed amount of gas, having sufficiently low density, is inversely proportional to its pressure."
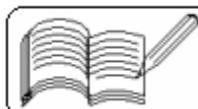
$\therefore$ $V \propto \dfrac{1}{P}$ (for fixed amount and fixed temperature)

$\therefore$ $PV = $ constant

Figure shows P $\rightarrow$ V curves for some real gas at three different temperatures obtained experimentally (shown by continuous lines) and theoretically using Boyle's law (shown by broken lines). From the graphs, it can be seen that real gas follows Boyle's law at high temperature and low pressure.

$T_1 > T_2 > T_3$
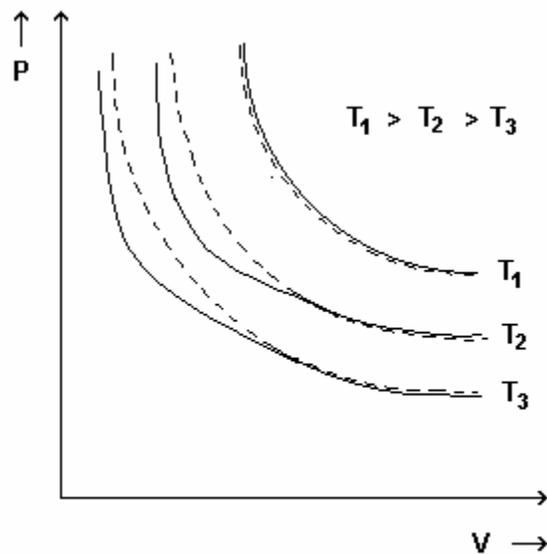
Graph of P $\rightarrow$ V

Charles' and Gay-Lussac's law:

"At constant pressure, the volume of a given amount of gas, having low density, is proportional to its absolute temperature."

$\therefore$ $V \propto T$ (for fixed amount and fixed pressure of gas) $\therefore$ $\dfrac{V}{T}$ = constant

Equation of state for an ideal gas:

Combining Boyle's and Charles' laws, $\dfrac{PV}{T}$ = constant (for a given amount of gas).

Also, the volume of gas is proportional to its amount at constant temperature and pressure.

$\therefore$ $\dfrac{PV}{T}$ = μR,   or $PV = \mu RT$ ...   .   (1)

    where μ represents the number of moles and
       R is universal gas constant = 8.314 J (mol)$^{-1}$ K^{-1} = 1.986 Cal (mol)$^{-1}$ K^{-1}.

A gas obeying the equation $PV = \mu RT$ at all pressures and temperatures is known as an ideal gas. No real gas behaves as an ideal gas under all the circumstances. However, at high temperature and at low pressure, i.e., at low density, real gas behaves like an ideal gas and obeys the above ideal gas law equation. As the thermodynamic state can be fixed using the above equation, it is called the equation of state for an ideal gas.

Avogadro's number:

"The number of constituent particles (atoms or molecules) contained in one mole of gas is called Avogadro's Number (N_A)."

The value of N_A is the same in all elements and is equal to 6.023×10^{23} (mol)$^{-1}$.

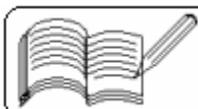If M g of gas has N molecules and M_0 is the molecular weight of gas, then

Number of moles of gas, μ = $\dfrac{N}{N_A}$ = $\dfrac{M}{M_0}$.

Different forms of equation of state of an ideal gas:

$PV = \dfrac{N}{N_A} RT = N \dfrac{R}{N_A} T = NkT$ ...   .   (2)

Here, $\dfrac{R}{N_A}$ = k = 1.38×10^{-23} J (molecule)$^{-1}$ K^{-1} (Boltzmann's constant)

$\therefore$ P = $\dfrac{N}{V}$ k T = n k T, ...   (3)

where $n = \dfrac{N}{V}$ = number of molecules per unit volume of the container, which is also called the number density of the molecules.

$\therefore$ $n = \dfrac{P}{kT}$ [from equation (3)]

Now, $PV = \mu RT = \dfrac{M}{M_0} RT$

$\therefore$ $P = \dfrac{M}{V} \cdot \dfrac{1}{M_0} RT = \dfrac{\rho}{M_0} RT$ ...   .   (4),   where $\rho = \dfrac{M}{V}$ = density of gas

Equations (1), (2), (3) and (4) are different forms of the equation of state of an ideal gas.

Avogadro's hypothesis:

"At constant temperature and pressure, the number of molecules in gases having the same volume is the same."

11.2 Kinetic theory of gases

Macroscopic physical quantities of a gas like pressure, temperature, etc. can be understood from the interrelationships between its microscopic quantities. This is discussed in the kinetic theory of gases based on the following postulates.

Molecular model of ideal gas: Postulates:

(1) A gas is made up of microscopic particles called molecules which may be monoatomic or polyatomic. If only one element is present in a gas, all its molecules are same and chemically stable.

(2) The molecules of a gas can be considered as perfectly rigid spheres or particles devoid of internal structure.

(3) The molecules are in continuous random motion colliding with each other and with the walls of the container.

(4) The molecules of a gas follow Newton's laws of motion.

(5) The number of molecules in a gas is very large. This assumption justifies randomness of their motion.

(6) The total volume of all the molecules of a gas is negligible as compared to the volume of the vessel containing the gas.

(7) Intermolecular forces act only when two molecules come close to each other or collide.

(8) The collision between the molecules and between the molecules and the wall of the container are elastic. The impact time of collision is negligible as compared to the time between successive collisions. Kinetic energy is conserved in an elastic collision. During the impact time of collisions, kinetic energy before collision is momentarily converted into potential energy but is again reconverted into the same amount of kinetic energy after the collision. Hence kinetic energy of the gas can be considered to be its total mechanical energy.

11.3 Pressure of an ideal gas

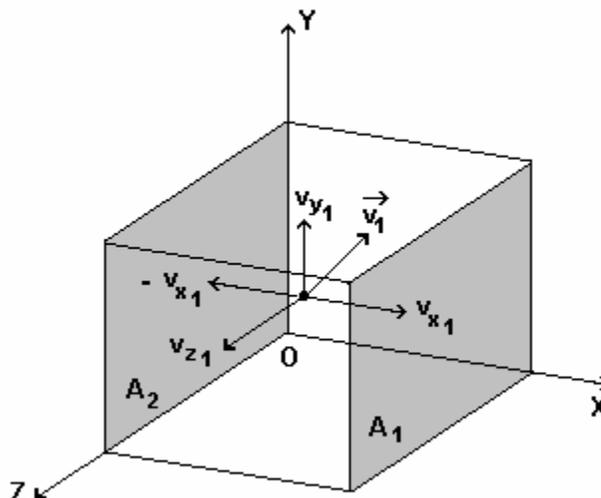Suppose an ideal gas is filled in a cubic container having elastic walls having each side of length, l.

$\therefore$ area of each wall = l^2.

Let N = number of molecules having velocities

$\vec{v_1}$, $\vec{v_2}$, $\vec{v_3}$, ,..., $\vec{v_N}$ at some instant and

   m = mass of each molecule.

Now consider opposite walls A_1 and A_2 of the container perpendicular to X-axis.

Let the molecule '1' have velocity $\vec{v_1}$ with its components, v_{x_1}, v_{y_1} and v_{z_1} along X-axis, Y-axis and Z-axis respectively.

When this molecule collides elastically with the wall A_1, its velocity along X-axis gets reversed and becomes $- v_{x_1}$. But y and z components of its velocity do not change.

The x-component of momentum of the molecule before collision is $p_i = m v_{x_1}$

The x-component of momentum of the molecule after collision is $p_f = - m v_{x_1}$

$\therefore$ the change in momentum of the molecule due to this collision is

$\Delta p = p_f - p_i = - m v_{x_1} - m v_{x_1} = - 2 m v_{x_1}$

$\therefore$ by the law of conservation of momentum, the wall gains momentum $2 m v_{x_1}$ in the direction of +ve X-axis.

Now, the molecule returning after colliding with A_1, collides with the wall A_2 and without making any other collision on its path, collides again with the wall A_1. Between these two collisions with the wall A_1, it travels a distance $2 l$ with velocity v_{x_1} along X-axis.

$\therefore$ time between two successive collisions, $t = \dfrac{2 l}{v_{x_1}}$

$\therefore$ number of collisions per second $= \dfrac{v_{x_1}}{2 l}$

$\therefore$ momentum gained by the wall per second = force, $F_1 = 2 m v_{x_1} \times \dfrac{v_{x_1}}{2 l} = \dfrac{m v_{x_1}^2}{l}$
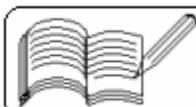
∴ total force on the wall due to all the N number of molecules

$$F = \sum_{i=1}^{n} \left[\frac{m\, v_{x_i}^2}{l} \right] = \frac{m}{l} \sum_{i=1}^{n} \left[v_{x_i}^2 \right]$$

∴ pressure on the wall, $P = \dfrac{Force}{Area} = \dfrac{F}{l^2} = \dfrac{m}{l^3} \sum_{i=1}^{n} \left[v_{x_i}^2 \right]$

$$= \frac{mN}{l^3} \sum_{i=1}^{n} \left[\frac{v_{x_i}^2}{N} \right]$$

$$= \frac{mN}{V} \sum_{i=1}^{n} \left[\frac{v_{x_i}^2}{N} \right] \qquad (\,V = l^3 = \text{volume of the container}\,)$$

$$\therefore \quad P = \rho < v_x^2 > \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where, $\dfrac{mN}{V} = \rho = $ density of gas

and $\displaystyle\sum_{i=1}^{n} \dfrac{v_{x_i}^2}{N} = < v_x^2 > = $ average of the squares of x-components of molecules.

Now, as the number of molecules is very large and their motion is random,

$$< v^2 > = < v_x^2 > + < v_y^2 > + < v_z^2 > \qquad \text{and} \quad < v_x^2 > = < v_y^2 > = < v_z^2 >$$

$$\therefore \quad < v^2 > = 3 < v_x^2 > \qquad \text{and} \quad < v_x^2 > = \frac{1}{3} < v^2 >$$

Putting this value of $< v_x^2 >$ in equation (1),

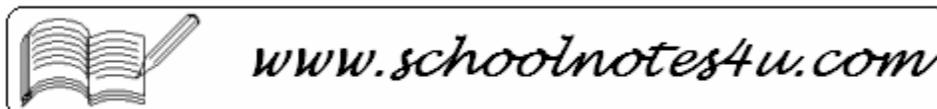$$P = \frac{1}{3} \rho < v^2 > \qquad \ldots \quad \ldots \quad \ldots \quad (2)$$

[This equation gives the pressure of an ideal gas.]

rms speed v_{rms} :

The square root of mean speed of molecules, also known as mean molecular speed,

$< v^2 >$ is called root mean square speed, v_{rms} .

From equation (2), $v_{rms} = \sqrt{< v^2 >} = \sqrt{\dfrac{3P}{\rho}}$

11.4 Kinetic energy and temperature

Pressure of an ideal gas is given by the equation,

$$P = \frac{1}{3} \rho <v^2>$$

$$\therefore \quad PV = \frac{1}{3} \rho V <v^2> = \frac{1}{3} M <v^2> \qquad (\text{as } \rho V = M \text{ is the total mass of gas.})$$

$$= \frac{1}{3} \mu M_0 <v^2>, \text{ where } \mu = \text{ number of moles of gas and}$$

$$M_0 = \text{ molecular weight of gas.}$$

Comparing this equation with $PV = \mu RT$ (ideal gas law equation), we get

$$\frac{1}{3} \mu M_0 <v^2> = \mu RT \qquad \therefore \quad M_0 <v^2> = 3 RT$$

$$\therefore \quad \frac{1}{2} M_0 <v^2> = \frac{3}{2} RT \quad \dots \ (1) \text{ which is the mean translational kinetic energy of 1 mole of}$$

gas and is proportional to the absolute temperature of gas.

$$\therefore \quad v_{rms} = \sqrt{\frac{3RT}{M_0}} \quad \dots \ (2)$$

Dividing equation (1) by Avogadro number, N_A,

$$\frac{1}{2} \frac{M_0}{N_A} <v^2> = \frac{3}{2} \frac{R}{N_A} T$$

$$\therefore \quad \frac{1}{2} m <v^2> = \frac{3}{2} kT \quad \dots \ (3) \quad [\, m = \text{ mass of a molecule, } k = \text{ Boltzmann's constant.}\,]$$

This is the mean translational kinetic energy per molecule of the gas and is proportional to the absolute temperature of the gas. It does not depend on pressure, volume or type of gas.

$$\therefore \quad v_{rms} = \sqrt{\frac{3kT}{m}} \quad \dots \ (4)$$

This equation shows that at a given temperature, the speed of lighter molecules is more as compared to that of heavier molecules.
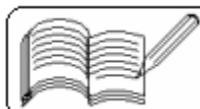
Dalton's law of partial pressure

Suppose a mixture of μ_1, μ_2, ..., moles of different ideal gases, mutually inert, is filled in a container of volume V at temperature T and pressure P and μ is the total number of moles.

$$\therefore \quad PV = \mu RT = (\mu_1 + \mu_2 + \dots) RT$$

$$\therefore \quad P = \frac{\mu_1 RT}{V} + \frac{\mu_2 RT}{V} + \dots = P_1 + P_2 + \dots ,$$

where P_1, P_2, ... are the partial pressure of the gases in the mixture.

Thus, the total pressure of the mixture of ideal gases, mutually inert, is the sum of their partial pressures. The partial pressure of any gas of the mixture is same as the pressure of that gas at the same temperature when it alone is filled in the container having the same volume.

11.5 Maxwell's law of molecular speed distribution

Gas molecules perform random motion with different speeds in different directions. James Clerk Maxwell gave molecular speed distribution law for a sample of gas containing N molecules as

$$N_v \, dv = 4 \pi N \left(\frac{m}{2 \pi k T} \right)^{\frac{3}{2}} e^{-\frac{m v^2}{2 k T}} v^2 \, dv ,$$

where,   N = total number of gas molecules
         Nv = number of molecules per unit speed interval
     $N_v \, dv$ = number of molecules having speed interval, dv
         m = mass of a molecule
         k = Boltzmann's constant
         T = absolute temperature

The graph shows the number of molecules per unit speed interval, N_v versus speed, v for oxygen gas at two different temperatures.
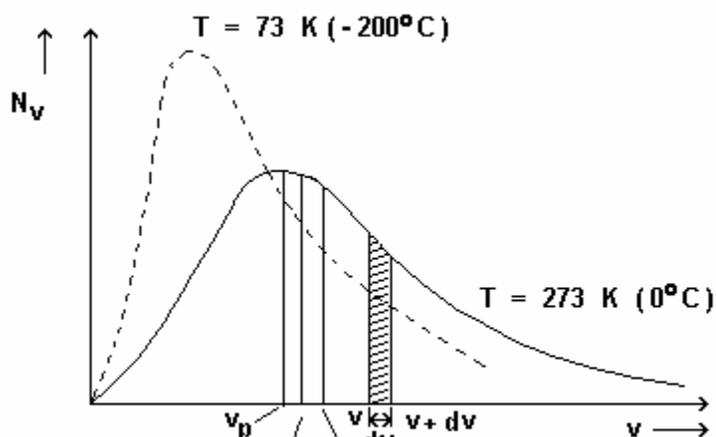
The total number of molecules, N is given by

$$N = \int_0^\infty N_v \, dv$$

and the average speed of molecules of the gas, each of mass m, at temperature T is

Graph of $N_V \rightarrow v$ for oxygen

$$< v > = \frac{1}{N} \int_0^\infty v \, N_v \, dv = \sqrt{\frac{8 k T}{\pi m}} = 1.59 \sqrt{\frac{k T}{m}}$$

$$v_{rms} = \sqrt{< v^2 >} = \sqrt{\frac{3 k T}{m}} = 1.73 \sqrt{\frac{k T}{m}}$$

Most probable speed (v_p): The speed possessed by the maximum number of molecules is called the most probable speed, v_p.

When $v = v_p$, $\frac{d}{dv} \left[4 \pi N \left(\frac{m}{2 \pi k T} \right)^{\frac{3}{2}} e^{-\frac{m v^2}{2 k T}} v^2 \right]_{v_p} = 0$ $\therefore$ $v_p = \sqrt{\frac{2 k T}{m}} = 1.41 \sqrt{\frac{k T}{m}}$

Thus, $v_p : < v > : v_{rms} = 1 : 1.128 : 1.224$.

11.6 Law of equipartition of energy

The average kinetic energy of each monoatomic molecule of a gas in a container is,

$$< E > = \frac{1}{2} m < v_x^2 > + \frac{1}{2} m < v_y^2 > + \frac{1}{2} m < v_z^2 > = \frac{3}{2} kT$$

But, $< v_x^2 > = < v_y^2 > = < v_z^2 >$

∴ $< E > = \frac{3}{2} m < v_x^2 > = \frac{3}{2} kT$

∴ $\frac{1}{2} m < v_x^2 = \frac{1}{2} kT$

Thus, the energy associated with each possible independent motion of a molecule in a container is $\frac{1}{2} kT$.

Now, consider diatomic gas molecules. They perform rotational and vibrational motion besides translational motion. The rotational motion of such a molecule is possible in two different ways, i.e., about two mutually perpendicular axes both passing through the mid-point of a line joining the molecules and perpendicular to the line as shown in the figure. For polyatomic gas molecules, such a motion can occur about three mutually perpendicular axes.
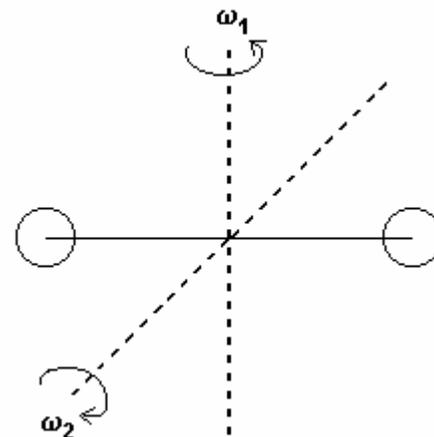
The atoms of a diatomic molecule perform oscillations also due to interatomic forces. Thus, a diatomic molecule possesses total energy comprising of three different types of energy:

(1) Translational kinetic energy,
$$E_t = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2),$$
(2) Rotational kinetic energy,
$$E_r = \frac{1}{2} I_1 \omega_1^2 + \frac{1}{2} I_2 \omega_2^2 \text{ and}$$
(3) Vibrational energy,
$$E_v = \frac{1}{2} \mu v^2 + \frac{1}{2} kx^2,$$ where the first and the second terms are the potential and kinetic energy respectively of the vibrator, μ is the reduced mass and k is the force constant of the system.

The number of quadratic terms for different motions appearing in the expression of total energy of a molecule are called degrees of freedom of the system. It is 3 for a monoatomic molecule, 5 for a non-vibrating diatomic molecule and 7 if it is vibrates.

Law of equipartition of energy states that the average energy of a molecule in a gas associated with each degree of freedom is (1 / 2) k T where k is Boltzmann's constant and T is the absolute temperature.
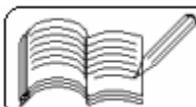
11.7 Mean free path

The linear distance traveled by a molecule of gas with constant speed between two successive collisions (with molecules) is called free path. Mean free path is the average of such free paths.

The path of random motion of a gas molecule is shown in the figure. The molecule moves on a straight path between two successive collisions, the length of which is called free path. But on collision, the direction and magnitude of its velocity changes.
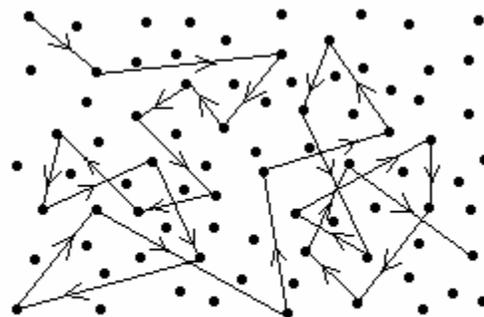
Path of motion of a molecule of a gas

Consider that one molecule of a gas moves with average speed $\bar{v}$ while other molecules are stationary. Its diameter is d.

During its motion on a straight path, it will not collide with a molecule which is at a perpendicular distance d from the straight path along which the centre of the molecule moves. Hence, we can imagine a cylinder around its path of radius d or diameter 2d such that the molecules outside this cylinder will not collide with the moving molecule.

In time t, the molecule will sweep the imaginary cylinder of cross-sectional area, πd^2, and length $\bar{v}t$. Thus, it will pass through the cylinder of volume $\pi d^2 \bar{v}t$ in time t. If n is the number of molecules per unit volume, the moving molecule will undergo $n\pi d^2 \bar{v}t$ collisions in time t.
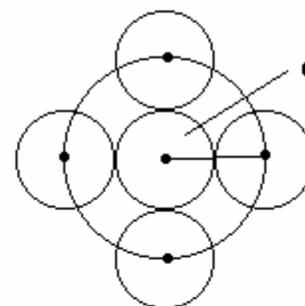
Sphere of collision of diameter 2d

The mean free path $\bar{l}$ is the average distance between two successive collisions.

$\therefore$ mean free path $= \dfrac{\text{distance travelled by the molecule}}{\text{total number of collisions}}$

     in time t.

$\therefore \quad \bar{l} = \dfrac{\bar{v}t}{n\pi d^2 \bar{v}t} = \dfrac{1}{n\pi d^2}$

In this derivation, the other molecules were assumed to be stationary. With rigorous analysis it can be shown that when the motion of all the molecules is considered, then the mean free path works out to be

$\bar{l} = \dfrac{1}{\sqrt{2}\, n\pi d^2}$
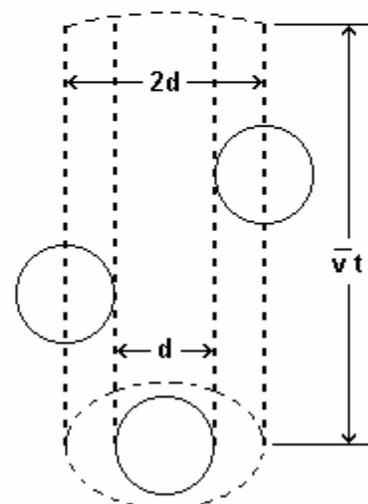
Imaginary cylinder of length $\bar{v}t$ and radius d