

ASSUMPTIONS of Kinetic Theory:

1. A gas consists of a large number of tiny particles called molecules.
2. The molecules are rigid and perfectly elastic spheres of very small diameters
3. All the molecules of the same gas are identical in shape, size and mass
4. Actual volume occupied by gas molecules is very small compared to the total volume occupied by the gas
5. The molecules are always in a state of random motion i.e. they are moving in all possible directions with all possible velocities. This state is also called as molecular chaos
6. Due to their random motion the molecules constantly collide with each other and also with the walls of the container. Such collisions are perfectly elastic i.e. there is no loss of kinetic energy during the collisions.
7. Between two successive collisions, a molecule travels in a straight line with constant velocity. It is called free path.
8. The time taken for collision is very small as compared to the time required to cover free path between two successive collisions.

NOTE: At low pressure or high temperature a real gas behaves close to an ideal gas.

Definitions:

Mean Free Path:

The distance travelled by the molecules between successive collisions with constant velocity in a straight line is called the free path. The average distance travelled by a gas molecule between two successive collisions is known as the mean free path.

Let $\lambda_1, \lambda_2, \dots, \lambda_N$ be the free path, then mean free path

$$\lambda = \frac{\lambda_1 + \lambda_2 + \dots + \lambda_N}{N}$$

NOTE: Higher the density, more the collisions and smaller the λ
Smaller the size of molecule, less the chance of collision hence larger the λ
 λ depends inversely to d^2 , where d : diameter of molecule

$$\lambda = \frac{1}{\sqrt{2} d^2 (N/V)}, N: \text{no of molecule}, V: \text{Volume}$$

Mean Velocity (Average Velocity) \bar{v} :

Mean velocity is defined as the arithmetic mean of all the velocities of the gas molecules of an ideal gas.

Consider N molecules of an ideal gas enclosed in a container.

Let v_1, v_2, \dots, v_N be their velocities, then

$$\bar{v} = \frac{v_1 + v_2 + \dots + v_N}{N}$$

Mean Square Velocity \bar{v}^2 :

The average value of the squares of the velocities of all molecules is known as mean square velocities.

Consider N molecules of an ideal gas enclosed in a container.

Let v_1, v_2, \dots, v_N be their velocities, then

$$\bar{v}^2 = \frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}$$

Root Mean Square Velocity (v_{RMS}):

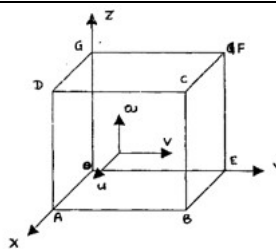
It is defined as the square root of the mean square velocity of the molecules of an ideal gas.

Consider N molecules of an ideal gas enclosed in a container.

Let v_1, v_2, \dots, v_N be their velocities, then

$$v_{RMS} = \sqrt{\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}}$$

EXPRESSION FOR PRESSURE EXERTED BY A GAS



Consider an ideal gas, which is enclosed in a cubical container having each side of length L .
Let, m = the mass of each molecule
 N = number of molecules of gas
 M = the total mass of gas = mN
 A = face area of cube = L^2
 ρ = density of gas = (M/V)

The molecules of the gas are moving in all possible directions with all possible velocities. Let $v_1, v_2, v_3, \dots, v_N$ be the velocities of the molecules. Let $(v_{x1}, v_{y1}, v_{z1}), (v_{x2}, v_{y2}, v_{z2}), (v_{x3}, v_{y3}, v_{z3}), \dots, (v_{xN}, v_{yN}, v_{zN})$ respectively by the X, Y and Z components of their velocities.

Let us consider a molecule having velocity v_1 . Then, $v_1^2 = v_{x1}^2 + v_{y1}^2 + v_{z1}^2$

Consider the motion of molecule along X axis.

Its momentum before colliding the wall ABCD = $m v_{x1}$

Its momentum after colliding the wall ABCD = $-m v_{x1}$

The molecule now travels with velocity $-u_1$ and collides with the wall EFGO.

Between the two successive collisions with the same surface, the molecules cover a distance $2L$. Hence in 1 second, the number of collisions of the molecule with the surface ABCD is $v_{x1}/2L$

Total momentum imparted to wall ABCD in one second = change in momentum in 1 collision \times number of collisions per second

Thus, Rate of change of momentum of wall ABCD = $2m v_{x1} \cdot (v_{x1}/2L) = m v_{x1}^2/L$

Total rate of change of momentum all molecules along X-axis = $(m v_{x1}^2/L + m v_{x2}^2/L + \dots + m v_{xN}^2/L)$

According to Newton's Second Law Rate of change of momentum is the force applied

$$F_x = \sum_{i=1}^N \frac{m v_{xi}^2}{L}$$

The pressure exerted on each wall perpendicular to the X-axis is

$$P_x = \frac{F_x}{L^2} = \sum_{i=1}^N \frac{m v_{xi}^2}{L^3}$$

Similarly pressure exerted on the Y and Z axis are

$$P_y = \frac{F_y}{L^2} = \sum_{i=1}^N \frac{m v_{yi}^2}{L^3}, \quad P_z = \frac{F_z}{L^2} = \sum_{i=1}^N \frac{m v_{zi}^2}{L^3}$$

All molecules are free to move in all possible directions $P_x = P_y = P_z = P$

Therefore, $P = (P_x + P_y + P_z)/3$

$$P = \frac{1}{3} \frac{m}{L^3} \sum_{i=1}^N (v_{xi}^2 + v_{yi}^2 + v_{zi}^2)$$

But, $v_1^2 = v_{x1}^2 + v_{y1}^2 + v_{z1}^2, v_2^2 = v_{x2}^2 + v_{y2}^2 + v_{z2}^2, \dots, v_N^2 = v_{xN}^2 + v_{yN}^2 + v_{zN}^2$

$$P = \frac{1}{3} \frac{m}{L^3} \sum_{i=1}^N v_i^2 = \frac{1}{3} \frac{mN}{L^3} \sum_{i=1}^N \frac{v_i^2}{N}$$

$$\text{But, } \sum_{i=1}^N \frac{v_i^2}{N} = \bar{v}^2 = \text{mean square velocity of gas and } L^3 = V = \text{volume of gas}$$

$$P = \frac{1}{3} \frac{mN}{V} \bar{v}^2 = \frac{1}{3} \frac{M}{V} \bar{v}^2 = \frac{1}{3} \rho \bar{v}^2$$

where M = mass of the gas and ρ = density of gas

Relation between Kinetic Theory of gases and absolute Temperature (OR average KE per molecule):

Consider a gas of volume V and N molecules each of mass m.

Mass of gas M = mN

According to kinetic theory, $P = \frac{1}{3} \rho v_{RMS}^2 = \frac{1}{3} \frac{M}{V} v_{RMS}^2$

Thus, $PV = \frac{1}{3} Mv_{RMS}^2$

$PV = \frac{1}{3} mN v_{RMS}^2$

$PV = \frac{1}{3} N (\frac{1}{2}mv_{RMS}^2) = \frac{1}{3} N(\text{avg KE per molecule}) \dots\dots(i)$

The internal energy of the gas is only kinetic since potential energy is zero due to no intermolecular attraction.

$E = N \cdot \frac{1}{2} m \overline{v^2}$ where E: Average Total energy

and $\frac{E}{N} = \text{energy per molecule} = \frac{1}{2} m \overline{v^2}$

Thus, $PV = \frac{2}{3} E$... by substituting the above in eqn (i)

$nRT = \frac{2}{3} E$, But $n = \frac{N}{N_A}$ where N_A is the Avogadro's number

$\frac{N}{N_A} RT = \frac{2}{3} E$, But $\frac{R}{N_A} = k_B$ the Boltzmann constant

Thus, $Nk_B T = \frac{2}{3} E$, Hence $\frac{E}{N} = \frac{3}{2} k_B T$

Thus average Energy (kinetic) per molecule is proportional to absolute temperature of the gas.

NOTE: KE per mole = KE per molecule x No. of molecules in a mole

$$= \frac{3}{2} k_B T N_A = \frac{3}{2} RT$$

KE of a gas per unit volume:

Consider an ideal gas enclosed in a cylinder having volume V. Let M be its total mass and $\overline{v^2}$ be the mean square velocity of its molecules. The pressure exerted by the gas is given by $P = \frac{1}{3} \frac{M}{V} \overline{v^2}$

$$\text{Therefore, } M \overline{v^2} = 3PV, \quad \frac{M \overline{v^2}}{2} = \frac{3PV}{2}$$

$$\text{Thus, KE per unit volume} = \frac{3P}{2}$$

RMS Velocity

Consider one mole of an ideal gas enclosed in a cylinder of volume V. Let M be the total Mass (=n.Mo, where n: number of moles, Mo is its Molecular weight). Let $\overline{v_{RMS}}$ be the RMS velocity.

$$P = \frac{1}{3} \frac{M}{V} \overline{v^2}, \text{ Thus } \overline{v^2} = \frac{3PV}{M} = \frac{3nRT}{M}, \text{ Since } PV = nRT$$

$$\text{thus, } \overline{v_{RMS}} = \sqrt{\frac{3nRT}{M}} = \sqrt{\frac{3RT}{M_0}}$$

$$\text{thus, } \overline{v_{RMS}} \propto \sqrt{T}$$

Mayers Relationship

Consider n mole of an ideal gas enclosed in a cylindrical vessel fitted with a weightless and frictionless piston.

When the gas is heated from T to T+dT and the piston is not allowed to move then all the heat supplied (dQ) will be utilized in increasing its internal energy (KE or temperature) only (dU).

Thus $dQ = dU = nC_v dT$ where C_v is called the molar specific heat capacity of the gas at constant volume.

Now, we heat it to the same temperature but this time allowing the piston to move and hence we are heating under constant pressure conditions.

Thus part of the heat will be utilized in doing work of expansion against the piston and rest will be internal energy of the gas (increasing its KE or temperature)

$$dQ' = dU + dW$$

Since we are heating it up to the same temperature, thus, $dU = nC_v dT$

Thus, $nC_p dT = nC_v dT + P \cdot dV$

$$nC_p dT = nC_v dT + nRdT \quad \text{where } P \cdot dV = nRdT \text{ (ideal gas)}$$

$$C_p = C_v + R$$

$$C_p - C_v = R \text{ (Mayer's Relation)} \quad R : \text{universal gas constant}$$

Thus, $C_p > C_v$

In terms of calories we write it as $C_p - C_v = R/J$, where J is mechanical equivalent of heat

NOTE: In terms of the principal specific heat (C_p and C_v)

$$M_0 C_p - M_0 C_v = R \quad \text{where } M_0 : \text{Molecular weight}$$

$$C_p - C_v = R/M_0$$

$$C_p - C_v = r \quad \text{where } r = \text{specific gas constant} = R/M_0$$

$$\text{or } C_p - C_v = r/J$$

Degree of Freedom

The total number of coordinates or independent quantities required to describe the position and configuration of the system.

$$\text{d.f.} = 3N - k$$

$$\text{Monoatomic} : N = 1; k = 0; \text{d.f.} = 3$$

$$\text{Diatomic} : N = 2; k = 1; \text{d.f.} = 5$$

$$\text{Triatomic} : N = 3; k = 3; \text{d.f.} = 6 \text{ (triangular)}$$

$$N = 3; k = 2; \text{d.f.} = 7 \text{ (linear)}$$

Law of Equipartition of Energy (not in syllabus)

Any dynamical system in thermal equilibrium, the energy is equally distributed among its various d.f.'s and energy associated with each d.f. is $\frac{1}{2} k \cdot T$

$$\text{Proof: KE/molecule} = \frac{1}{2} m v^2 = \frac{3}{2} k \cdot T$$

$$\frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) = \frac{3}{2} k \cdot T$$

$$\frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 = \frac{3}{2} k \cdot T$$

$$\text{KE}_x/\text{molecule} + \text{KE}_y/\text{molecule} + \text{KE}_z/\text{molecule} = \frac{3}{2} k \cdot T$$

But, $\text{KE}_x = \text{KE}_y = \text{KE}_z$ (due to random motion)

$$\text{KE}_x / \text{molecule} = \text{KE}_y / \text{molecule} = \text{KE}_z / \text{molecule} = \frac{1}{2} k \cdot T$$

C_p, C_v, γ for Mono, Di, Tri, Poly atomic

Monoatomic: d.f. = 3

$$\text{Total Internal Energy per mole (U)} = \text{d.f.} \times (\text{KE/molecule}) \times N_A$$

$$= 3 \left(\frac{1}{2} k T \right) N_A$$

$$= \frac{3}{2} RT$$

$$C_v = dU/dT = \frac{3}{2} R; \quad C_p = C_v + R = \frac{5}{2} R; \quad \gamma = C_p/C_v = 5/3 = 1.67$$

Diatomic: d.f. = 5

$$\text{Total Internal Energy per mole (U)} = \text{d.f.} \times (\text{KE/molecule}) \times N_A$$

$$= 5 \left(\frac{1}{2} k T \right) N_A$$

$$= \frac{5}{2} RT$$

$$C_v = dU/dT = \frac{5}{2} R; \quad C_p = C_v + R = \frac{7}{2} R; \quad \gamma = C_p/C_v = 7/5 = 1.4$$

Triatomic: d.f. = 6 (triangular)

$$\text{Total Internal Energy per mole (U)} = \text{d.f.} \times (\text{KE/molecule}) \times N_A$$

$$= 6 \left(\frac{1}{2} k T \right) N_A$$

$$= 3 RT$$

$$C_v = dU/dT = 3R; \quad C_p = C_v + R = 4R; \quad \gamma = C_p/C_v = 4/3 = 1.33$$

Triatomic: d.f. = 7 (Linear)

$$\text{Total Internal Energy per mole (U)} = \text{d.f.} \times (\text{KE/molecule}) \times N_A$$

$$= 7 \left(\frac{1}{2} k T \right) N_A$$

$$= \frac{7}{2} RT$$

$$C_v = dU/dT = \frac{7}{2} R; \quad C_p = C_v + R = \frac{9}{2} R; \quad \gamma = C_p/C_v = 9/7 = 1.28$$

Polyatomic: d.f. = f

$$\text{Total Internal Energy per mole (U)} = \text{d.f.} \times (\text{KE/molecule}) \times N_A$$

$$= f \left(\frac{1}{2} k T \right) N_A$$

$$= \frac{f}{2} RT$$

$$C_v = dU/dT = \frac{f}{2} R; \quad C_p = C_v + R = \left(\frac{f}{2} + 1 \right) R; \quad \gamma = C_p/C_v = 1 + \frac{2}{f}$$