

Kinetic molecular theory of gases was first developed by Daniel Bernoulli (1738) and subsequent progress was made by Joule, Clausius, Maxwell and Boltzmann within 1848-1898.

Assumptions:

- This theory consists of the following assumptions:
- ① The gas is composed of very small discrete particles, now called molecules. For a gas, the mass and size of the molecules are same and different for different gases.
 - ② The molecules are moving at random in all directions with variety of speeds. Some are very fast while others are slow.
 - ③ Due to random motion, the molecules are executing collision with the walls of the container (wall-collision) and also with themselves (intermolecular collisions). These collisions are perfectly elastic, and so there occurs no loss of kinetic energy or momentum of the molecules by these collisions. Speed of the molecules remain same due to wall-collisions but may change in intermolecular collisions.
 - ④ The gas molecules are assumed to be point masses, i.e., their size is very small in comparison to the distance they travel.
 - ⑤ There exists no intermolecular attractions especially at low pr., i.e., one molecule can exert pr. independent of the influence of the other molecules.
 - ⑥ The pressure exerted by a gas is due to the incessant and uniform wall-collisions of the molecules. Higher the frequency of the wall-collisions, greater will be the pr. of the gas. This explains Boyle's Law since when vol. is reduced, wall-collisions become more frequent and the pr. is increased.
 - ⑦ Though the molecular speeds are constantly changing due to intermolecular collisions, average kinetic energy (\bar{E}) of the molecules remains fixed at a given temp. This explains Charles's Law that when temp. is increased, \bar{E} is increased, velocities (as $E = \frac{1}{2}mv^2$) are increased, wall-collisions become more frequent and violent, so pr. is increased when vol. is kept const. or vol. is increased when pr. is kept const.

Idea of root-mean-square speed (C_{RMS}) :-

Let in a gas of N molecules, N_1 have speed C_1 , N_2 molecules have speed C_2 , N_3 molecules have speed C_3 and so on, then

$$\begin{aligned}\bar{E} &= \frac{N_1 E_1 + N_2 E_2 + N_3 E_3 + \dots}{N} \\ &= \frac{1}{N} \left[N_1 \times \frac{1}{2} m C_1^2 + N_2 \times \frac{1}{2} m C_2^2 + N_3 \times \frac{1}{2} m C_3^2 + \dots \right] \\ &= \frac{1}{2} m \left[\frac{N_1 C_1^2 + N_2 C_2^2 + N_3 C_3^2 + \dots}{N} \right] = \frac{1}{2} m C_{RMS}^2\end{aligned}$$

The term within the bracket is called C_{RMS}^2 (mean-square-speed, \bar{C}^2) and root-mean-square speed is defined as

$$C_{RMS} (= \sqrt{\bar{C}^2}) = \sqrt{\frac{N_1 C_1^2 + N_2 C_2^2 + N_3 C_3^2 + \dots}{N}}$$

Concept of Temp. and Kinetic theory:-

This speed (C_{RMS}) is more fundamental than average speed, \bar{C} since it originates spontaneously from the average kinetic energy of the molecules and it depends on the thermodynamic parameter, temp (T) (Postulate 7).

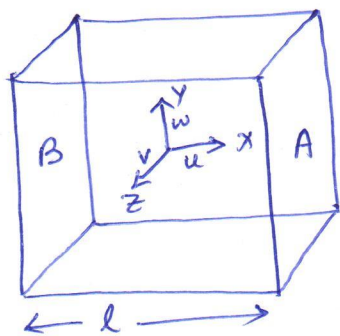
Thus Kinetic theory of gases can provide a concept of temp. (T). Average kinetic energy (\bar{E}) is a measure of temp. Higher the average kinetic energy of a gas, greater will be its temperature. When the molecules are at rest (i.e. $\bar{E} = 0$), the temp. will also be 0K.

Formulation of kinetic equation:- $PV = \frac{1}{3} m N C_{RMS}^2$

The postulates of the kinetic theory enable us to calculate the pr. of a gas in terms of molecular quantities.

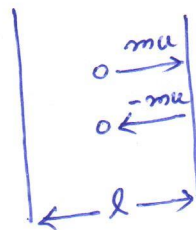
Let us take a cube of edge length l containing N molecules of a gas of molecular mass m and RMS speed is C at temp. T and pr. P . Let N_1 molecules have speed C_1 , N_2 molecules have

Speed C_2 , N_3 molecules have speed C_3 , and so on.



Volume of the cube,
 $V = l^3$

Total surface area
 $= 6l^2$



change of momentum
for the collision

$$= mu - (-mu) \\ = 2mu$$

Let us concentrate our attention to a single molecule among N_1 that have resultant speed C_1 and the component velocities are u , v and w along the x -, y - and z -axis respectively.

$$\text{So, } C_1^2 = u^2 + v^2 + w^2$$

The molecule will collide walls A and B with the component velocity u and other opposite faces by v and w . change of momentum of the molecule along x -direction for a single collision $= mu - (-mu) = 2mu$. The number of collisions suffered by the molecule in unit time between the two opposite walls $= \frac{u}{l}$ and so the rate of change of momentum for the above type collisions $= 2mu \times \frac{u}{l} = \frac{2mu^2}{l}$.

Similarly, along y - and z -directions, the rate of change of momenta of the molecule are $\frac{2mv^2}{l}$ and $\frac{2mw^2}{l}$, respectively.

Total rate of change of momentum of the molecule

$$= \frac{2m}{l} (u^2 + v^2 + w^2) = \frac{2mC_1^2}{l}$$

For similar N_1 molecules, the rate of change of momentum $= \frac{2mN_1C_1^2}{l}$

Taking all the molecules of the gas, the total rate of change of

$$\begin{aligned} \text{momentum} &= \frac{2mN_1C_1^2}{l} + \frac{2mN_2C_2^2}{l} + \frac{2mN_3C_3^2}{l} + \dots \\ &= \frac{2mN}{l} \left(\frac{N_1C_1^2 + N_2C_2^2 + N_3C_3^2 + \dots}{N} \right) = \frac{2mN\bar{C}^2}{l} \end{aligned}$$

According to the Newton's 2nd law of motion, rate of change of momentum due to wall-collision is equal to the force developed on the walls of the gas container. Thus,

$$P \times 6l^2 = \frac{2mN\bar{c}^2}{l}, \text{ but } l^3 = V, \text{ volume of the gas in the cube.}$$

$$P(\text{Pr}) \times \text{Area}(6l^2) = F(\text{force})$$

So, the kinetic equation of the gas is :

$$P \times V = \frac{1}{3} m N \bar{c}^2$$

Again the equation is $P = \frac{1}{3} \left(\frac{mN}{V} \right) \bar{c}^2$

Newton's 2nd law of motion:
The acceleration of an object as produced by a net force is directly proportional to the magnitude of net force, in the same direction as the net force, and inversely proportional to the mass of the object.
but $\frac{mN}{V} = d$ to the mass of the object

density of the gas at the given temp. and Pr. So, another form of the kinetic eqn. is $P = \frac{1}{3} d \bar{c}^2$. This c is RMS speed of the gas molecules. These equations are also valid for any shape of the gas container other than cubic one.

Expression of root-mean square speed:

Let us apply the kinetic eqn. for 1 mole ideal gas. In that case, $mN = mN_A = M$, the molar mass of the gas and the ideal gas eqn. for 1 mole is $PV = RT$

Putting in the kinetic eqn., we have $RT = \frac{1}{3} M \bar{c}^2$.

$$\text{So, } c (= \sqrt{\bar{c}^2}) = \sqrt{\frac{3RT}{M}}$$

This shows that RMS speed depends on the molar mass (M) and temp (T) of the gas.

Expression of Average Kinetic Energy (\bar{E}):

The kinetic eqn. can be written as : $PV = \frac{2}{3} N \left(\frac{1}{2} m \bar{c}^2 \right)$.

But $\frac{1}{2} m \bar{c}^2 = \bar{E}$, Average kinetic energy of the molecules. Thus, considering 1 mole ideal gas, $RT = \frac{2}{3} N_A \bar{E} \Rightarrow \bar{E} = \frac{3}{2} \left(\frac{R}{N_A} \right) T$

Thus, the expression of average kinetic energy of the gas molecules at temp. T is given as : $\bar{E} = \frac{3}{2} kT$, where k = Boltzmann const.

$$= \frac{R}{N_A} = 1.38 \times 10^{-16} \text{ erg molecule}^{-1} \text{K}^{-1}$$

For 1 mole gas, the KE is $\bar{E} = \frac{3}{2} RT$

For n mole of the gas, the KE is $E = \frac{3}{2} nRT$

\bar{E} depends on the temp. only and does not depend on the nature of the gas. Thus, most light gas H_2 and very heavy gas UF_6 both have same average KE at a given temp.

Deduction of the gas laws from kinetic equation:-

From kinetic eqn., we have $PV = \frac{2}{3} N_A \bar{E}$, but

$\bar{E} \propto T, \Rightarrow \bar{E} = K' T$. Thus, $PV = \left(\frac{2}{3} N_A K'\right) T = \text{const.} \times T$

This eqn. provides necessary deduction of the gas laws such as Boyle's law, Charles law, etc. Deduction of Avogadro's law is given here only.

Let us consider two gases under same T , P and V . Thus,

$$PV = \frac{1}{3} m_1 N_1 C_1^2 = \frac{1}{3} m_2 N_2 C_2^2$$

$$\Rightarrow m_1 N_1 C_1^2 = m_2 N_2 C_2^2 \quad \text{--- (1)}$$

Again, the two gases have the same average KE at the given T .

$$\text{So, } \bar{E}_1 = \bar{E}_2 \Rightarrow \frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2 \Rightarrow m_1 C_1^2 = m_2 C_2^2 \quad \text{--- (2)}$$

So, dividing the eqn. (1) by the eqn. (2), we have $N_1 = N_2$. It means that equal volumes of all gases at the same T and P contain equal number of molecules and it is Avogadro's Law.

Graham's law of diffusion can also be deduced. The rate of diffusion of a gas (r_d) is directly proportional to the speed of the gas. Thus, $r_d \propto C$, but $C = \sqrt{\frac{3RT}{M}} \Rightarrow r_d \propto \sqrt{\frac{3RT}{M}}$.

This shows that at a given T , $r_d \propto \sqrt{\frac{1}{M}}$. Thus, at a given temp., the rate of diffusion is inversely proportional to the square root of molar mass of the gas and this is Graham's Law of diffusion.