KINETIC THEORY

KINETIC THEORY OF AN IDEAL GAS

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The kinetic theory of gases is like having a huge bunch of tiny particles (molecules) that are always moving randomly. When it's not too extreme, the molecules are pretty far apart, much more than their size. So, most of the time, they move in straight lines without bothering each other because they don't have strong forces between them. Sometimes, though, they get close, feel these forces, and their speed changes. We call these close encounters "collisions." Molecules keep bumping into each other or the container walls and bounce back, like a rubber ball. We say these collisions are elastic, meaning they don't lose any energy. With this idea, we can figure out how gas pressure works based on the kinetic theory.

We start with the concept that gas molecules are always moving around randomly, like they're playing a game of tag. They keep bumping into each other and the container walls. When they bump into each other or the walls, they bounce back without losing any energy. This means that the overall energy they have stays the same. And, like always, the total push they have (momentum) also stays the same.

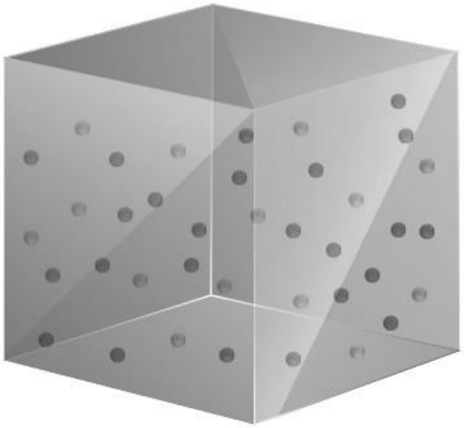
Dalton's Law of Partial Pressure

When the temperature stays the same, if you have a mix of two or more gases that don't react with each other, the total pressure they create in a certain space is just the sum of the pressures each of those gases would make on their own in that space.

Imagine you have a container filled with several gases that don't react with each other. The pressure inside the container is not changing, and we want to find the total pressure all those gases together create (PT). This is how we calculate it:

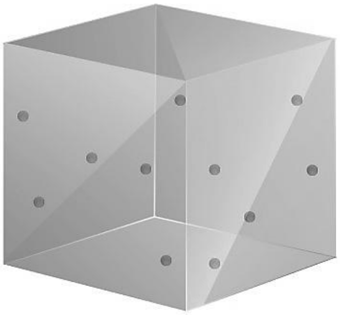
$P_T = P_1 + P_2 + P_3 + \cdots + P_n$

Where, $P_1, P_2, P_3, \dots, P_n$ represents the partial pressures of n individual gases.

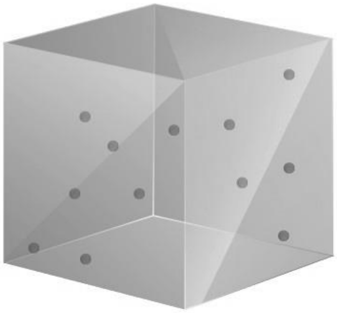


The pressure of one gas is linked to how many moles of that gas there are. So, if there are more moles of a gas, it will have a higher pressure.

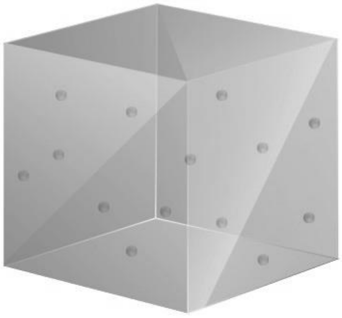
If you have a mix of several gases that don't react with each other, you can think of them as each having their own pressure, and together they make up the total pressure in the system, all at the same temperature.



P_1



P_2



P_3

For each gas, we can use the ideal gas equation, and we assume that the space each gas takes up is the same as the container's volume (V).

The partial pressure of the first gas, $P_1V = n_1RT$
The partial pressure of the second gas, $P_2V = n_2RT$
The partial pressure of the nth gas, $P_nV = n_nRT$

For a mixture of two gases inside a container

Imagine you have a mix of gases with a total pressure calledP_T. Each gas in the mix has its own pressure, like P_1 andP_2. And there are different amounts of each gas, like n_1 andn_2."

For the mixture, we can write the ideal gas equation as follows:

$$\mathrm{P_TV = (n_1 + n_2)RT}$$

Where,
V is the volume of the container.
R is the universal gas constant.

Since the individual gases are occupying the whole container, we can write the ideal gas equation for them as follows:
The partial pressure of the first gas, $P_1V = n_1RT$
the partial pressure of the second gas, $P_2V = n_2RT$
on comparing the given equations, we get,

$$P_TV = n_1RT + n_2RT$$

$$\Rightarrow P_TV = P_1V + P_2V$$

$P_T = P_1 + P_2$

This is the expression for Dalton's law for a mixture of two non-reacting gases.

Question.

Three containers of same volume contain three different gases. The masses of the molecules are m1, m2, and m3, and the numbers of the molecules in the respective containers are N1, N2, and N3. The gas pressures in the containers are P1, P2, and P3 respectively. All the gases are now mixed and put in one of the containers. What will be the pressure (P) of the mixture?

(A) $P < P_1 + P_2 + P_3$

(B) $P = \frac{P_1+P_2+P_3}{3}$

(C) $P = P_1 + P_2 + P_3$

(D) $P > P_1 + P_2 + P_3$

Solution.

When you mix all three gases together, the total pressure of the mix is just the sum of the pressures each gas had on its own.

Each container's pressure shows how much pressure one gas has because the amount of gas molecules in each container doesn't change, even when they're mixed together.

HenceP_1,P_2 and P_3 represent the respective partial pressures of the gases.

Volume of the gas mixture = Volume of the container = V

From Dalton's law of partial pressure,
$P_T = P_1 + P_2 + P_3$

$\Rightarrow P = P_1 + P_2 + P_3$

Thus, option (C) is the correct answer.

Diffusion

Diffusion means that gas molecules naturally spread out and mix with each other when there's a difference in their concentrations.

- When a liquid or gas can move on its own, it naturally spreads out from places where there's a lot of it to places where there's less. This difference in amounts is called a "concentration gradient."

- For example, if you put a drop of ink in a glass of water, the ink will quickly spread toward the clear water, where there's less ink. This happens because the liquid wants to even out its concentration.

- We can also smell food cooking from far away because the smell spreads through the air by the same process, called diffusion.

Effusion

Effusion is when gas molecules move from a place with lots of pressure to a place with less pressure, like a vacuum, through a tiny hole without bumping into each other. In this situation, the hole they pass through is really small.

- Think of a balloon that shrinks because the gas inside it has slowly leaked out through tiny holes. This is an example of effusion.

- If you have a container with gas in two parts, and you make a tiny hole in the divider between them, the gas will move from the side with higher pressure to the side with lower pressure. That's also an example of effusion.

Graham's law of effusion

The speed at which a gas escapes is linked to how heavy it is. If a gas is light, its molecules are more likely to escape quickly through a hole compared to a gas with heavy molecules. This happens because lighter gas moves faster.

$$\therefore r \propto \frac{1}{\sqrt{\rho}}$$

Where, r is the rate of effusion and ρ is the density of the gas molecule.
The density of a gas is directly proportional to its molar mass (M).

$$\rho \propto M$$

So, the expession for the rate of effusion changes as follows:

$$r \propto \frac{1}{\sqrt{M}}$$

$$r = \frac{k}{\sqrt{M}}$$

Where, k is the proportionality constant.

Graham's Law of Diffusion

When you let two gases mix with each other, and they're at the same pressure and temperature, how fast they mix depends on how heavy the molecules in the gas are. Lighter gas molecules mix faster.

Imagine two containers with gas, and you connect them with a valve. When you open the valve, the gases will start to mix together.

Relation between the rates of diffusion of gases is,

$$r = \frac{\mathrm{k}}{\sqrt{\rho}}$$

Hence, $r_1 = \frac{k}{\sqrt{\rho_1}}$ $and\ r_2 \frac{k}{\sqrt{\rho_2}}$

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

$\because \rho \propto M$

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_2}{M_1}}$$

Here, r_1 and r_2 represent the rates of diffusion of the respective gas molecules, ρ_1 and ρ_2 are densities of the respective gases, and M_1 and M_2 represent the molar masses of the respective gases.

Ideal Gas Equation

For n moles of an ideal gas,
PV = nRT
Here, P is the pressure exerted on the gas, V is the volume occupied by the gas, R is the universal gas constant and T is the temperature of the gas.

The equation describing ideal gases concerning the constituent gas molecules.

We have,
N_A molecules of gas = 1 mol of gas

1 molecule of gas = $\frac{1}{N_A}$ mol of gas

Substituting the value of moles in the equation PV = nRT, we get the following:

$$PV = \frac{1}{N_A} RT = \left(\frac{R}{N_A}\right) T = kT$$

Here, $\frac{R}{N_A}$ is the Boltzmann constant (k) and it is defined as the gas constant per mole.

$$k = \frac{R}{N_A} = \frac{8.314}{6.023 \times 10^{23}} = 1.38 \times 10^{-23}\ JK^{-1}$$

For N molecules of gas,
$PV = NkT$

The ideal gas equation expressed with reference to the mass of the gas.

1 mol of an ideal gas = M gram
(Where, M = Molar mass of the ideal gas)

1 gram of gas = $\frac{1}{M}$ mol

Substituting the value of moles in the equation PV = nRT, we get the following:

$$PV = \frac{1}{M}RT = \left(\frac{R}{M}\right)T = rT$$

Here, $\frac{R}{M}$ is known as the specific gas constant (r) and it is defined as the gas constant per gram of gas.

$$\therefore r = \frac{R}{M}\ J\ g^{-1}\ K^{-1}$$

For m gram molecules of gas,
PV = mrT

The ideal gas equation framed in relation to gas density.

We have,

PV = nRT

Moles of the gas (n) = $\frac{Mass\ of\ the\ gas\ (in\ gram)}{Molar\ mass\ of\ the\ gas\ (in\ gram)} = \frac{m}{M}$

$$PV = \left(\frac{m}{M}\right)RT$$

$$PM = \left(\frac{m}{V}\right)RT$$

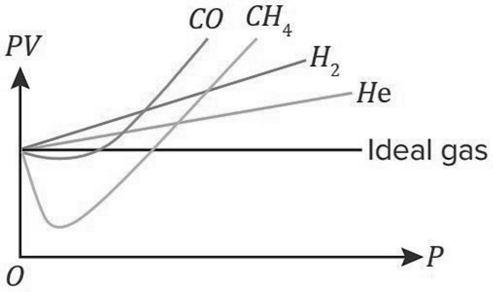
$$PM = \rho RT$$

Where, ρ is the density of the ideal gas.

Real Gases

Gases that don't always follow the ideal gas law perfectly at any temperature and pressure are called real gases.

The graph in the picture shows how different real gases act when you change the temperature and pressure. In the graph, you can notice that methane (CH4) shifts down the most at low pressure because it's the heaviest among the gases shown.



The Departure of Actual Gases from Ideal Conduct

- If the graph of pressure (P) against product of pressure and volume (PV) is a straight line that doesn't tilt, it means the gas behaves like an ideal gas.

- When the PV-P graph shifts upwards compared to the ideal gas line, it's called a positive deviation.

- When the PV-P graph shifts downwards compared to the ideal gas line, it's called a negative deviation.

Comparing Pressure-Volume (P-V) Graphs of a Real Gas and an Ideal Gas

When we examine a constant pressure for both real and ideal gases by drawing a straight line along the V-axis in a high-pressure area, we observe that

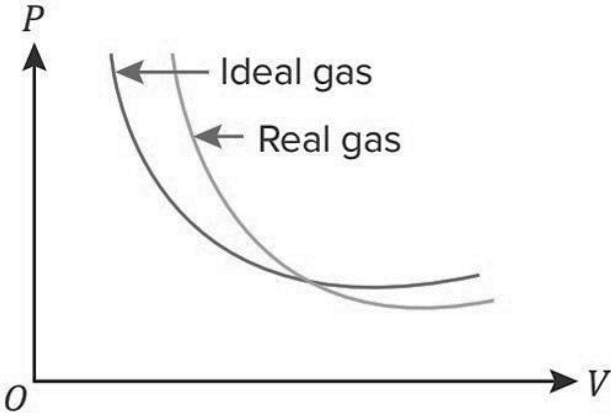
$V_{real} > V_{ideal}$

This signifies that at higher pressures, the influence of repulsive forces results in a larger volume for real gases.

Conversely, when we examine a constant pressure for both real and ideal gases in a low-pressure region by drawing a straight line parallel to the V-axis, we find that

$V_{real} < V_{ideal}$

This indicates that at lower pressures, the prevalence of attractive forces results in a smaller volume for real gases.



What accounts for the deviation of real gases from ideal gas behavior?

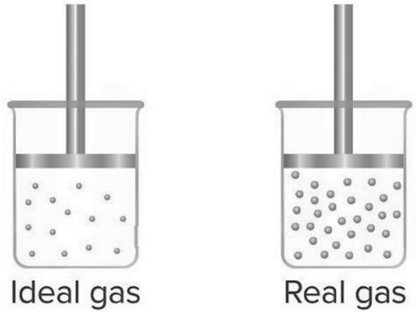
The following points explain why real gases behave differently from ideal gases:

- Ideal gases are assumed to have very weak interactions between their molecules, but in reality, gas molecules do interact with each other through weak attractive forces.
- Ideal gases are also assumed to have no volume, but in reality, they do occupy some space."

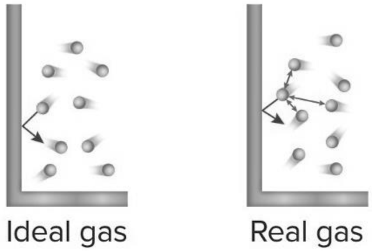
Volume occupied by the gas = Volume of the container
However, in reality, the gas molecules do occupy some volume. Thus, for a real gas,
Volume occupied by the gas ≠ Volume of the container
The volume available for a real gas will be less than V.

Real Gas vs Ideal Gas

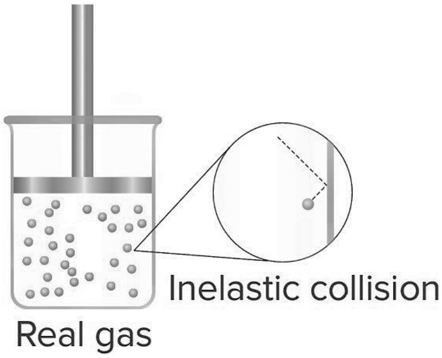
- Real gas particles take up a noticeable amount of space inside the container.
- Ideal gases cannot turn into liquids, but when real gases become liquids, they occupy a definite volume.



- Real gases have forces that pull their molecules together (attraction).
- But with ideal gases, we assume these forces are so tiny that we can ignore them.



- In ideal gases, when gas molecules bump into each other, we think none of their energy is lost, like in a perfectly bouncy collision.
- But in real gases, when molecules hit the container walls, some energy is lost, like in a less bouncy collision.



The Van der Waals Gas Equation

For ideal gases,
PV = nRT

$P_{ideal}V_{ideal} = nRT$

Because real gases have intermolecular forces and their molecules take up space, we can't use this equation for them.

$P_{ideal}V_{ideal} \neq nRT$

So, to use the ideal gas equation for real gases, we have to make some changes. Van der Waals came up with a modified version of the ideal gas equation, and it's named after him, the Van der Waals gas equation.

To get the Van der Waals gas equation, we made some adjustments to the ideal gas equation:

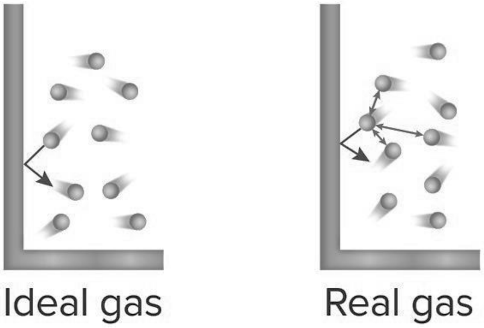
- Pressure correction
- Volume correction

Pressure correction

When a gas molecule hits the container wall, it gets pulled a bit by its nearby gas buddies due to weak forces between them. As a result, it slows down during the collision with the container.

So, there's less momentum passed, and as a result, the force on the container's wall becomes weaker.

Therefore, real gases produce lower pressure.



$P_{ideal} > P_{real}$

$P_{ideal} = P_{real} + dP$

Here, dP is the pressure-correction term.

$dP = \frac{an^2}{V^2}$

Where, $\propto$ = Van der Waals constant

And, a $\propto$ Attractive force

$P_{ideal} = P_{real} + \frac{an^2}{V^2}$

Volume correction

In an ideal gas, the space where gas molecules can move freely is the entire container volume because we've assumed that the gas molecules themselves don't take up any space.

V_{ideal} = Volume available for the free motion of gas = V_{free}

But in a real gas, some of the container space is taken up by the gas molecules themselves. So, there's less room for the gas to move around freely.

$V_{free} = V_{container} - V_{container}$

Volume of the container, $V_{container} = V$

Volume occupied by the gas molecules, $V_{container} = nd$

$V_{free} = V - nb$

Where, b = Volume of one mole of gas particles

And, b $\propto$ Size of the gas molecule

In this context, the term 'excluded volume' pertains to the spatial domain encompassed by the molecules constituting a real gas, a region that is inaccessible for the unrestrained mobility of the gas particles.

On substituting the terms of modified pressure and volume in the ideal gas equation, we get,

$P_{ideal}V_{ideal} = nRT$

$\left(P_{real} + \frac{an^2}{V^2}\right)(V - nb) = nRT$

This is the required Van der Waals gas equation. Here, $\left(\frac{an^2}{V^2}\right)$ is the pressure-correction term and (nb) is the volume-correction term.

Compressibility Factor (Z)

The deviation from ideal behavior can be quantified by utilizing the compressibility factor (Z).

Let us take a mole of an ideal gas. It will follow the ideal gas equation,
PV = nRT

For one mole of an ideal gas, n is equal to 1.
PV = RT

$\frac{PV}{RT} = 1$

So, the compressibility factor for the ideal gas is,

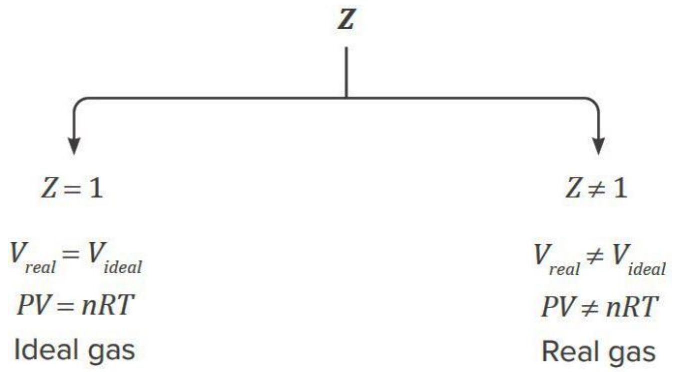
$Z = \frac{PV}{RT} = 1$

Compressibility factor can also be defined as the ratio of the observed volume of the gas to the calculated volume at the same values of n, T, and P.

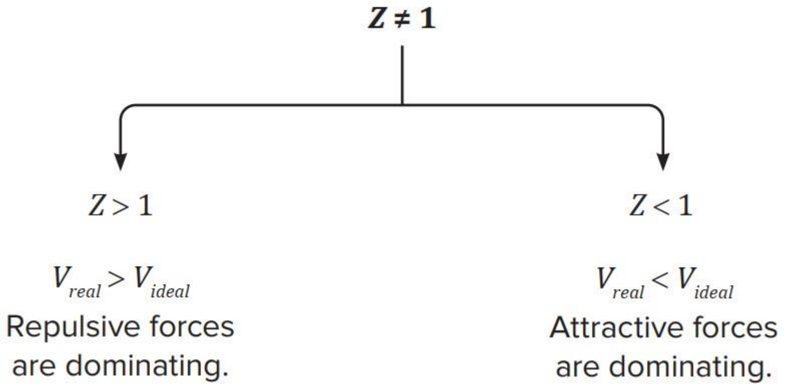
$Z = \frac{V_{real}}{V_{ideal}}$

Usually, for a gas, we can measure the volume in experiments, and we can also calculate what the volume should be using the ideal gas equation, which is $P_{ideal}\, V_{ideal}$ = nRT. This is done at the same pressure and temperature.

Different values of Z (For competitive exam)



For real gases, Z ≠ 1



The value of Z also tells us if we can turn a gas into a liquid.

- Ideal gases can't be turned into liquids.
- Real gases are hard to turn into liquids when Z is greater than 1, and it's easy to turn them into liquids when Z is less than 1." **(End here)**

Pressure of an Ideal Gas

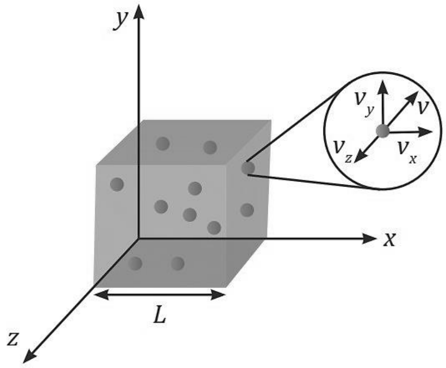
Imagine a cube-shaped container filled with gas. Inside, there are N gas molecules, and each molecule weighs m. Because the gas molecules move around randomly, their chances of moving in any direction are equal.

Since all the gas molecules are identical, let us select one molecule among them, moving within the container with a velocity denoted as 'v.' This velocity 'v' can be deconstructed into three constituent components aligned with the x, y, and z axes.

Instantaneous velocity, $\vec{v} = v_x\,\hat{\imath} + v_y\,\hat{\jmath} + v_z\,\hat{k}$

Since the probability of moving in every direction is the same,

So, $v_x = v_y = v_z$



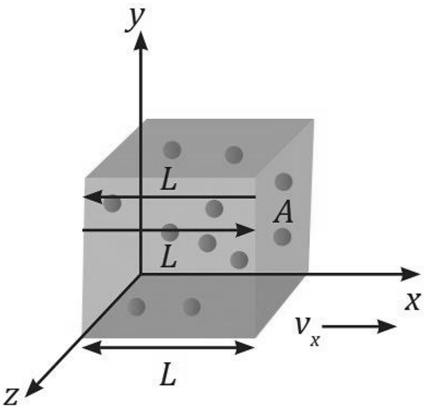
Time taken between two successive collisions

Imagine the molecule hitting one wall and then bouncing off to hit the opposite wall of the cube, which has a side length of L, along the x-axis.

The time it takes for the molecule to go from hitting wall A to hitting it again (Δt) can be calculated like this:

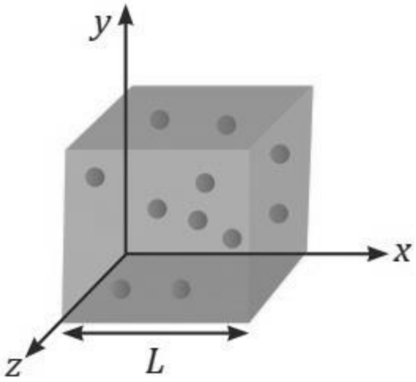
$$\Delta t = \frac{\textit{Distance travelled by the molecule between two successive collisions}}{\textit{Velocity of the molecule}}$$

$$\Delta t = \frac{2L}{v_x}$$



Change in momentum

Imagine that we consider the velocity in the direction of the positive x-axis as a positive value, and the velocity in the direction of the negative x-axis as a negative value.



Momentum before the collision, $p_i = mv_x$

Momentum of the molecule after the collision, $p_f = -mv_x$

Therefore, change in the momentum is given as follows:

$\Delta p = p_f - p_i$

$\Delta p = -mv_x - mv_x$

$\Delta p = -2mv_x$

Magnitude of change in the momentum, $|\Delta p| = 2mv_x$

The push or pressure exerted by a single molecule on a wall

$F_x = \frac{|\Delta p|}{\Delta t}$

$F_x = \frac{2mv_x \times v_x}{2L}$ $\left(\text{Since } \Delta t = \frac{2L}{v_x}\right)$

$F_x = \frac{m{v_x}^2}{L}$

Total force on wall for N molecules

Force due to first molecule, $F_{x_1} = \frac{mv_{x_1}^2}{L}$

Force due to second molecule, $F_{x_2} = \frac{mv_{x_2}^2}{L}$

.

Similarly, force due to Nth molecule, $F_{x_N} = \frac{mv_{x_N}^2}{L}$

Total force on the wall $\left(F_{x,\text{ net}}\right) = F_{x_1} + F_{x_2} + \ldots\ldots + F_{x_N}$

$$F_{x,\text{ net}} = \frac{mv_{x_1}^2}{L} + \frac{mv_{x_2}^2}{L} + \ldots\ldots + \frac{mv_{x_N}^2}{L}$$

$$F_{x,\text{ net}} = \frac{m}{L}\left[v_{x_1}^2 + v_{x_2}^2 + v_{x_3}^2 + \ldots\ldots + v_{x_N}^2\right]$$

Root mean square velocity along the x-axis is,

$$v_{x,rms} = \sqrt{\frac{v_{x_1}^2 + v_{x_2}^2 + v_{x_3}^2 + \ldots\ldots + v_{x_N}^2}{N}}$$

.

$$v_{x,rms}^2 = < v_x^2 > = \frac{v_{x_1}^2 + v_{x_2}^2 + v_{x_3}^2 + \ldots\ldots + v_{x_N}^2}{N}$$

$$v_{x_1}^2 + v_{x_2}^2 + v_{x_3}^2 + \ldots\ldots + v_{x_N}^2 = N < v_x^2 >$$

Substituting it in the force equation, it changes as follows:

$$F_{x,\text{ net}} = \frac{m}{L}\left[v_{x_1}^2 + v_{x_2}^2 + v_{x_3}^2 + \ldots\ldots + v_{x_N}^2\right]$$

$$F_{x,\text{ net}} = \frac{mN}{L} < v_x^2 >$$

We know that the probability of moving in every direction is the same,

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

Now, the magnitude of the net velocity is as follows:

$$< v^2 > = < v_x^2 > + < v_y^2 > + < v_z^2 > \quad . \quad .$$

$$< v^2 > = 3 < v_x^2 >$$

$$< v_x^2 > = \frac{< v^2 >}{3}$$

Substituting this value in the force equation, we get the following:

$$F_{x,\text{ net}} = \frac{mN}{L} < v_x^2 >$$

$$\Rightarrow F_{x,\text{ net}} = \frac{mN}{3L} < v^2 >$$

Pressure on the surface due to gas molecule

$$F_{x,\text{ net}} = \frac{mN}{3L} < v^2 >$$

Area of the surface, $A = L^2$

Pressure on the surface, $P = \frac{F_{\text{net}}}{A}$

$$P = \frac{mN < v^2 >}{3L \times L^2}$$

$$P = \frac{mN < v^2 >}{3V}$$

.

$< v^2 >=$ Mean square velocity of molecules

$\sqrt{< v^2 >} = v_{rms} =$ Root mean square velocity of molecules

$$P = \frac{1}{3}\frac{mN}{V}v_{rms}^2$$

We know, $N \times m = M =$ Net mass of gas

$$P = \frac{1}{3}\frac{M}{V}v_{rms}^2$$

Also, $\frac{M}{V} = \rho$

$$\therefore P = \frac{1}{3}\rho v_{rms}^2$$

Connection between Pressure and the Energy of Moving (Kinetic) Particles

Kinetic energy, $KE = \frac{1}{2}Mv_{rms}^2$

Also, $P = \frac{1}{3}\frac{M}{V}v_{rms}^2$

$$PV = \frac{1}{3}Mv_{rms}^2$$

For one mole of ideal gas, PV = RT,

$$\Rightarrow RT = \frac{1}{3}Mv_{rms}^2$$

$$\Rightarrow 3RT = Mv_{rms}^2$$

Dividing both sides by 2,

$$\frac{3RT}{2} = \frac{Mv_{rms}^{2}}{2}$$

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

Degree of Freedom (f)

The number of possible independent motions of a system is known as the degree of freedom of the system.