

# Kinetic theory of gases

## Most important question answers

**Question (1): State these gas laws and write their mathematical statements:**

- a. Boyle's law
- b. Charle's law
- c. Gay lussac's law
- d. Ideal gas equation
- e. Avogadro's law
- f. Graham's law of diffusion

### a. Boyle's Law:

- Statement: At constant temperature, the volume of a fixed amount of gas is inversely proportional to its pressure.
- Mathematical Statement:  $PV = k$ , where P is pressure, V is volume, and k is a constant.

### b. Charles's Law:

- Statement: At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature.
- Mathematical Statement:  $\frac{V}{T} = k$ , where V is volume, T is temperature in Kelvin, and k is a constant.

### c. Gay-Lussac's Law:

- Statement: At constant volume, the pressure of a fixed amount of gas is directly proportional to its absolute temperature.
- Mathematical Statement:  $\frac{P}{T} = k$ , where P is pressure, T is temperature in Kelvin, and k is a constant.

### d. Ideal Gas Equation:

- Statement: For a given amount of gas, the product of its pressure and volume is directly proportional to its absolute temperature.
- Mathematical Statement:  $PV = nRT$ , where P is pressure, V is volume, n is the number of moles of gas, R is the ideal gas constant, and T is temperature in Kelvin.

### e. Avogadro's Law:

- Statement: Equal volumes of gases, at the same temperature and pressure, contain equal numbers of molecules.
- Mathematical Statement:  $\frac{V}{n} = k$ , where V is volume, n is the number of moles of gas, and k is a constant.

### f. Graham's Law of Diffusion:

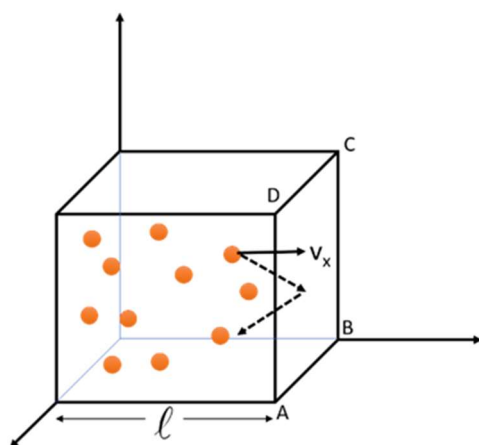
- Statement: The rate of diffusion of a gas is inversely proportional to the square root of its molar mass.
- Mathematical Statement: Rate  $\propto \frac{1}{\sqrt{M}}$ , where M is the molar mass of the gas.

### Question (2): Derive an expression for pressure exerted by an ideal gas.

Consider a cubical chamber of edge length  $\ell$  containing an ideal gas as shown. Let number of molecules per unit volume be  $n$ . Consider a molecule with velocity  $v$  with velocity components  $v_x$ ,  $v_y$  and  $v_z$ .

Momentum of this molecule before hitting wall ABCD =  $mv_x$

Since the collisions of an idea gas (according to KTG) are perfectly elastic so the momentum of the molecule after hitting the wall is  $-mv_x$  (negative sign because direction is opposite now)



Therefore, change in momentum =  $-mv_x - mv_x = -2mv_x$

So, momentum imparted to the wall =  $2mv_x$ .

Therefore, average momentum of that each molecule imparts to the wall is  $2m\bar{v}_x$

where  $\bar{v}_x$  is the average of velocity components of molecules in x direction

No of molecules that can hit the wall in time  $\Delta t$  is  $n\bar{v}_x\Delta t\ell^2$ , but since half of these molecules are moving away from the wall. Therefore, number of molecules that will actually hit

the wall in time  $\Delta t$  is  $\frac{1}{2}n\bar{v}_x\Delta t\ell^2$ .

So, total momentum imparted to wall in time  $\Delta t$  is  $\frac{1}{2}n\bar{v}_x\Delta t\ell^2 \times 2m\bar{v}_x = mn\bar{v}_x^2\Delta t\ell^2$

Therefore, force exerted on the wall =  $\frac{mn\bar{v}_x^2\Delta t\ell^2}{\Delta t} = mn\bar{v}_x^2\ell^2$

Therefore, pressure exerted by x component,  $P_x = \frac{\text{Force}}{\text{Area}} = mn\bar{v}_x^2\ell^2 = \frac{mn\bar{v}_x^2\ell^2}{\ell^2} = mn\bar{v}_x^2$ . Since the velocity of gas in all directions should be same due to its random motion, therefore,  $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2$

Since  $\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$  so we get  $\bar{v}^2 = 3\bar{v}_x^2 \Rightarrow \bar{v}_x^2 = \frac{1}{3}\bar{v}^2$

Therefore, we get  $P = \frac{1}{3}mn\bar{v}^2$ . Since  $mn = \rho$  (density of gas), therefore

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

### Question (3): Explain these various speeds of gas molecules:

- Root mean square speed
- Average speed.
- Most probable speed

#### Root Mean Square Speed (RMS Speed):

- The root mean square speed of gas molecules is the square root of the average of the squares of the velocities of all the molecules in a gas sample.

- Mathematically, the RMS speed ( $v_{\text{rms}}$ ) can be calculated using the formula:  $v_{\text{rms}} = \sqrt{\frac{3kT}{M}}$

where:

- $k$  is Boltzmann's constant ( $1.38 \times 10^{-23} \text{ J/K}$ ),
- $T$  is the temperature in Kelvin,
- $M$  is the molar mass of the gas in kilograms.

#### b. Average Speed:

- The average speed of gas molecules is the arithmetic mean of the velocities of all the molecules in a gas sample.
- It is calculated by summing up all the individual speeds of the molecules and dividing by the total number of molecules.
- The formula for the average speed ( $v_{\text{avg}}$ ) is dependent on the distribution of speeds, and it's usually related to the RMS speed.

#### c. Most Probable Speed:

- The most probable speed of gas molecules is the speed at which the greatest number of molecules in a gas sample have.
- It occurs at the peak of the Maxwell-Boltzmann speed distribution curve.
- The formula for the most probable speed ( $v_{\text{mp}}$ ) depends on temperature and is given by:

$$v_{\text{mp}} = \sqrt{\frac{2kT}{M}}$$

where  $k$ ,  $T$ , and  $M$  have the same meanings as in the RMS speed formula.

### Question (4): What is degree of freedom? How does it depend on atomicity of a gas?

the degree of freedom refers to the number of independent ways a particle or system can store energy or move in space. It essentially represents the number of independent coordinates needed to describe the state of a system.

For a gas molecule, the degree of freedom includes translational, rotational, and vibrational motion. The degree of freedom ( $f$ ) for a gas molecule can be calculated using the formula:

$$f = 3N - s$$

Where:

- $N$  is the total number of atoms or molecules in the gas.

- $s$  is the number of constraints on the motion of the gas molecules. Constraints can include fixed axes, fixed bond lengths, or other limitations on motion due to molecular structure.

The degree of freedom depends on the atomicity (the number of atoms per molecule) of the gas because it determines the number of independent ways a molecule can store energy or move.

### Question (5): What is law of equipartition of energy?

The law of equipartition of energy, also known as the equipartition theorem, is a principle in statistical mechanics that states that, in thermal equilibrium, each degree of freedom of a system in classical mechanics will, on average, have an energy of  $\frac{1}{2}kT$ , where  $k$  is Boltzmann's constant and  $T$  is the temperature in Kelvin.

### Question (6): Derive the values of $C_p$ and $C_p$ of a polyatomic gas.

Average energy available per molecule per degree of freedom =  $\frac{1}{2}k_B T$

If gas has  $n$  degrees of freedom, then average energy available per molecule,  $u = \frac{n}{2}k_B T$

$\therefore k_B = \frac{R}{N_A}$  where  $R$  is universal gas constant, therefore  $u = \frac{n}{2} \frac{R}{N_A} T$

So, average energy per mole  $U = \frac{n}{2} \frac{R}{N_A} T \times N_A = \frac{n}{2} RT$

Since

$$dQ = dU + PdV$$

At constant volume,  $dV = 0$  and  $dQ = C_v dT$

$$\therefore dU = C_v dT$$

$$\Rightarrow C_v = \frac{dU}{dT} = \frac{n}{2} R \frac{dT}{dT}$$

$$\Rightarrow C_v = \frac{nR}{2}$$

$$\therefore C_p = C_v + R$$

$$\Rightarrow C_p = \frac{nR}{2} + R = R \left( \frac{n}{2} + 1 \right)$$

$$\text{So, } \gamma = \frac{C_p}{C_v} = \frac{R \left( \frac{n}{2} + 1 \right)}{\frac{nR}{2}}$$

$$\Rightarrow \boxed{\gamma = 1 + \frac{2}{n}}$$

If the gas is monoatomic, then,  $n = 3$ , then  $\boxed{\gamma = 1 + \frac{2}{3} = \frac{5}{3}}$

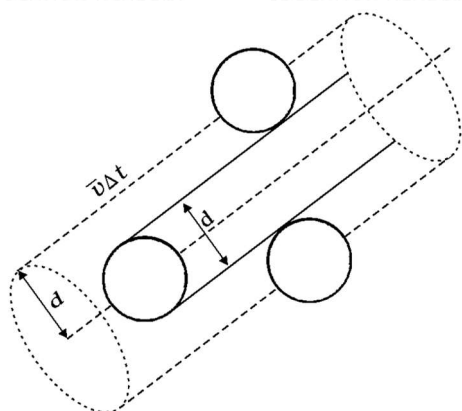
If the gas is diatomic,  $n = 5$ , then  $\gamma = 1 + \frac{2}{5} = \frac{7}{5}$

For triatomic gas linear molecule,  $n = 7$   $\gamma = 1 + \frac{2}{7} = \frac{9}{7}$

For triatomic non-linear molecule  $n = 6$ ,  $\gamma = 1 + \frac{2}{6} = \frac{4}{3}$

**Question (7): What is mean free path? Derive an expression for it.**

*It is the average distance travelled by a gas molecule between two successive collisions.*



Consider a gas having  $n$  molecules per unit volume. Let the diameter of each molecule be  $d$  and it is moving with velocity  $v$ . Now, it will hit only those molecules in time  $\Delta t$  whose centres are within a distance  $d$  from the centre of this molecule.

So, number of molecules that this molecule will hit in time  $\Delta t = n\pi d^2 v \Delta t$

Therefore, number of collisions per unit time =  $\frac{n\pi d^2 v \Delta t}{\Delta t} = n\pi d^2 v$

So, average time between two collisions =  $\frac{1}{n\pi d^2 v}$

Therefore, average distance between two collisions,

$$\lambda = \frac{1}{n\pi d^2 v} \times v$$

$$\Rightarrow \lambda = \frac{1}{n\pi d^2}$$

In this derivation we have assumed that other molecules are rest, which is not possible in reality. The actual result is

$$\lambda = \frac{1}{\sqrt{2}n\pi d^2}$$