PART 1: INTRODUCTION, MOLECULAR NATURE OF MATTER, IDEAL GAS EQUATION AND BASIC ASSUMPTIONS

1.1 LEARNING OBJECTIVES

After studying this part, students will be able to:

1. Understand the molecular nature of matter.
2. Explain the basic concepts of kinetic theory of gases.
3. Describe the assumptions of the kinetic theory of an ideal gas.
4. Understand the relationship between pressure and molecular motion.
5. Define an ideal gas and distinguish it from a real gas.
6. Use the ideal gas equation to solve numerical problems.
7. Understand the concepts of mole, Avogadro's number and molecular mass.
8. Explain the microscopic origin of gas pressure.

1.2 INTRODUCTION TO KINETIC THEORY OF GASES

The **kinetic theory of gases** explains the macroscopic properties of gases in terms of the motion and behaviour of their microscopic particles.

The macroscopic properties of a gas include:

- Pressure
- Volume
- Temperature
- Density
- Internal energy

According to kinetic theory, a gas consists of a very large number of tiny molecules that are in continuous random motion.

These molecules collide with one another and with the walls of the container. Their collisions with the container walls produce gas pressure.

The temperature of a gas is related to the average translational kinetic energy of its molecules.

Thus, kinetic theory establishes a connection between the microscopic motion of molecules and the measurable properties of a gas.

Example

When air is filled into a balloon, the air molecules move randomly in all directions. Their collisions with the inner surface of the balloon exert pressure on it.

The pressure of the gas tends to expand the balloon, while the tension in the stretched rubber tends to contract it.

1.3 MOLECULAR NATURE OF MATTER

Matter is composed of extremely small particles called atoms and molecules.

Depending on the nature of the substance, these particles may be:

- Atoms, as in helium and neon.
- Molecules, as in oxygen and nitrogen.
- Other microscopic particles appropriate to the substance.

The spacing and motion of these particles differ in solids, liquids and gases.

1.3.1 Solids

In solids:

1. Particles are closely packed.
2. The attractive forces between particles are generally strong.
3. Particles vibrate about their equilibrium positions.
4. Solids have a definite shape and volume under ordinary conditions.

1.3.2 Liquids

In liquids:

1. Particles are relatively close together.
2. Particles can move past one another.
3. Liquids have a definite volume but no definite shape.
4. Liquids take the shape of their containers.

1.3.3 Gases

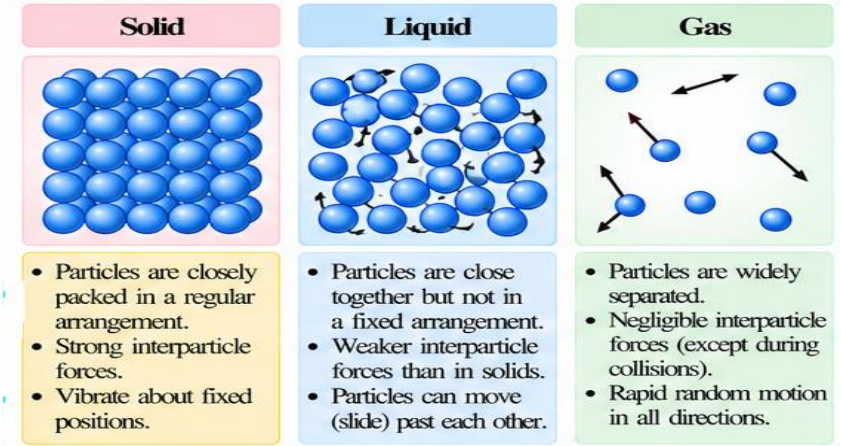
In gases:

1. Molecules are widely separated compared with their molecular size.
2. Molecules move continuously and randomly.
3. Intermolecular forces are usually negligible except during collisions in the ideal-gas approximation.
4. Gases do not have a definite shape or volume.
5. Gases expand to occupy the available space in a container.

Important Concept

The pressure and temperature of a gas arise from the collective behaviour of its molecules.
Pressure is associated with molecular collisions, while temperature is related to the average kinetic energy of random translational motion.

Figure 12.1: Molecular Arrangement in Solids, Liquids and Gases



1.4 WHAT IS AN IDEAL GAS?

An ideal gas is a theoretical gas whose molecules are assumed to have negligible volume and no intermolecular forces except during collisions.
An ideal gas obeys the equation:

$$\boxed{PV = nRT}$$

Where:

- P = pressure of the gas
- V = volume of the gas
- n = number of moles
- R = universal gas constant
- T = absolute temperature

The ideal-gas model is particularly useful for understanding the behaviour of gases at sufficiently low pressures and sufficiently high temperatures, where many real gases approximately follow ideal-gas behaviour.

1.4.1 Characteristics of an Ideal Gas

An ideal gas is assumed to have the following characteristics:

1. Its molecules are treated as point particles.
2. The total molecular volume is negligible compared with the volume occupied by the gas.
3. Molecules move continuously and randomly.
4. Molecules exert no intermolecular forces on one another except during collisions.
5. Collisions between molecules and with container walls are perfectly elastic.
6. The duration of a collision is negligible compared with the time between successive collisions.
7. Molecules obey Newton's laws of motion in the classical kinetic-theory model.
8. At a given temperature, the average translational kinetic energy is determined by the absolute temperature.

Important: A real gas only approximates an ideal gas under suitable conditions. No real gas perfectly satisfies every assumption of the ideal-gas model under all conditions.

1.5 BASIC ASSUMPTIONS OF THE KINETIC THEORY OF GASES

The kinetic theory of an ideal gas is based on the following assumptions.

1.5.1 Large Number of Molecules

A gas contains an enormous number of molecules.

The number of molecules in an ordinary sample is so large that statistical averages can be used to describe its behaviour.

1.5.2 Negligible Molecular Size

The molecules are treated as point particles.

Their individual volumes are assumed to be negligible compared with the total volume occupied by the gas.

1.5.3 Continuous Random Motion

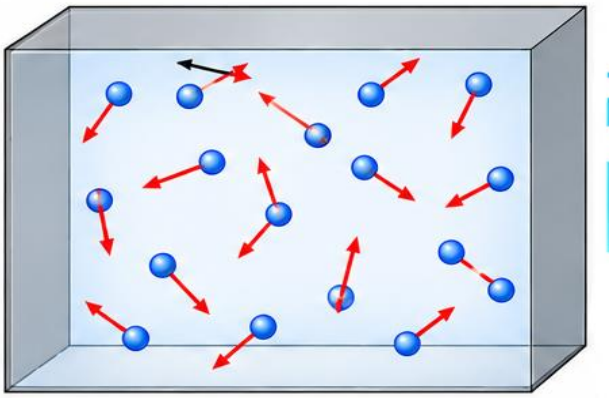
Gas molecules move continuously in random directions. At equilibrium, no direction is preferred on average. Therefore, the average velocity vector of the molecules is zero:

$$\bar{\vec{v}} = 0$$

However, their average speed and average kinetic energy are not zero.

This distinction is important because velocity is a vector quantity, whereas speed is a scalar quantity.

Figure 12.2: Random Motion of Gas Molecules



Gas molecules are in continuous random motion in all directions with different speeds.

1.5.4 Negligible Intermolecular Forces

In the ideal-gas approximation, intermolecular forces are neglected except during collisions. Consequently, between collisions, molecules move approximately in straight lines with constant velocities.

1.5.5 Elastic Collisions

Collisions between molecules and between molecules and the container walls are assumed to be perfectly elastic.

Thus, the total kinetic energy is conserved during an ideal collision.

1.5.6 Random Distribution of Molecular Velocities

At thermal equilibrium, molecular velocities are distributed randomly.

The gas has no net bulk motion when viewed in its rest frame.

For a gas in equilibrium, the average squares of the velocity components are equal:

$$\boxed{\overline{v_x{}^2} = \overline{v_y{}^2} = \overline{v_z{}^2}}$$

Since

$$v^2 = v_x{}^2 + v_y{}^2 + v_z{}^2$$

Taking the average gives:

$$\overline{v^2} = \overline{v_x{}^2} + \overline{v_y{}^2} + \overline{v_z{}^2}$$

Therefore,

$$\boxed{\overline{v_x{}^2} = \frac{\overline{v^2}}{3}}$$

Similarly,

$$\boxed{\overline{v_y{}^2} = \overline{v_y{}^2} = \frac{\overline{v^2}}{3}}$$

This result is important in deriving the expression for gas pressure.

1.6 MOLE, AVOGADRO'S NUMBER AND NUMBER OF MOLECULES

1.6.1 Mole

A mole is the amount of substance containing exactly:

$$\boxed{N_A = 6.02214076 \times 10^{23} molecules/mole}$$

specified elementary entities.

This number is called **Avogadro's constant**.

The elementary entities may be atoms, molecules, ions or other specified particles.

For school-level numerical problems, Avogadro's constant is often approximated as:

$$\boxed{N_A = 6.022 \times 10^{23} mol^{-1}}$$

1.6.2 Number of Molecules

If a gas contains n moles, the number of molecules is:

$$\boxed{N = nN_A}$$

Where:

- N = total number of molecules
- n = number of moles
- N_A = Avogadro's constant

$$\boxed{n = \frac{N}{N_A}}$$

1.6.3 Number of Moles from Mass

If the mass of a sample is m and the molar mass is M, then:

$$\boxed{n = \frac{m}{M}}$$

Here, m and M must be expressed in compatible units.

For example, if the mass is measured in grams, the molar mass should be expressed in grams per mole.

Combining the relations:

$$\boxed{N = \frac{mN_A}{M}}$$

This formula is useful for finding the number of molecules in a gas sample.

1.7 Universal Gas Constant

The universal gas constant is:

$$\boxed{R = 8.314\ Jmol^{-1}K^{-1}}$$

For many numerical problems, the value may be approximated as:

$$\boxed{R = 8.31\ Jmol^{-1}K^{-1}}$$

1.7.1 Ideal Gas Equation in Terms of Number of Molecules

We know that:

$$n = \frac{N}{N_A}$$

Substituting into the ideal gas equation:

$$PV = \frac{NRT}{N_A}$$

Rearranging:

$$PV = N\left(\frac{R}{N_A}\right)T$$

The Boltzmann constant is defined as:

$$\boxed{k_B = \frac{R}{N_A}}$$

Therefore,

$$\boxed{PV = Nk_BT}$$

Where:

$$\boxed{\boldsymbol{k_B = 1.381 \times 10^{-23} J/K}}$$

This form of the ideal gas equation is especially useful in kinetic theory because it directly relates macroscopic quantities to the number of molecules.

1.7.2 Two-State Form of the Ideal Gas Equation

For a fixed amount of an ideal gas:

$$\frac{P_1V_1}{T_1} = nR$$

And

$$\frac{P_2V_2}{T_2} = nR$$

Since n is constant:

$$\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$$

This relation is useful when a gas changes from one equilibrium state to another without any change in the amount of gas.

Temperature must be expressed in kelvin.

1.8 MICROSCOPIC ORIGIN OF GAS PRESSURE

Gas pressure is produced by the continuous collisions of gas molecules with the walls of their container.

Consider a gas enclosed in a cubical container.

Let:

- L = side length of the cube
- V = volume of the cube
- m = mass of each molecule
- v_x = x-component of the molecular velocity
- N = total number of molecules

The volume is:

$$\boxed{V = L^3}$$

Consider one molecule moving toward a wall perpendicular to the x-axis.

Before collision, its x-component of velocity is v_x.

For a perfectly elastic collision with the wall:

$$v_x \rightarrow -v_x$$

The change in momentum of the molecule is:

$$\Delta p_x = -mv_x - mv_x$$

Therefore,

$$\Delta p_x = -2mv_x$$

The magnitude of the momentum change is:

$$\boxed{|\Delta p_x| = 2mv_x}$$

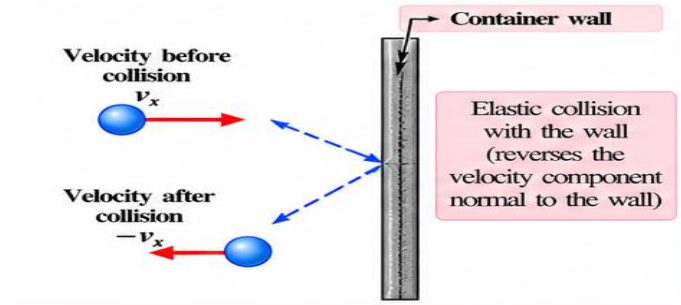
By Newton's third law, the wall receives an equal and opposite momentum change.
Thus, molecular collisions transfer momentum to the wall and exert a force on it.
For a large number of molecules, the combined effect of these collisions produces the measurable pressure of the gas.

Important Concept

Gas pressure is a macroscopic result of molecular momentum transfer to the container walls.

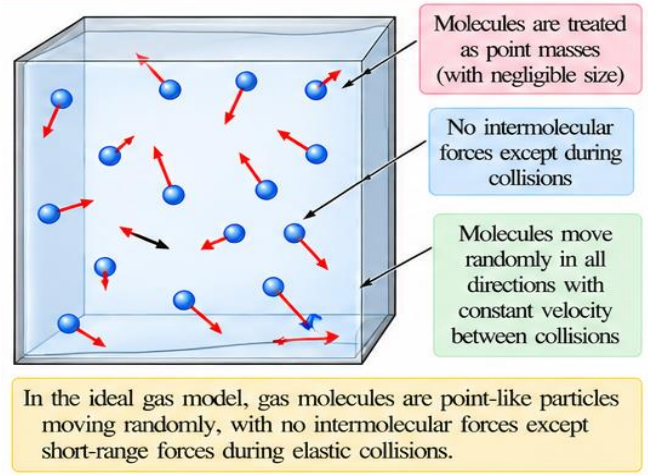
The complete mathematical derivation of the pressure equation will be developed in the next part.

Figure 12.3: Molecular Collisions with Container Walls



During collision, the molecule transfers momentum to the wall, producing a force and hence pressure.

Figure 12.4: Ideal Gas Model

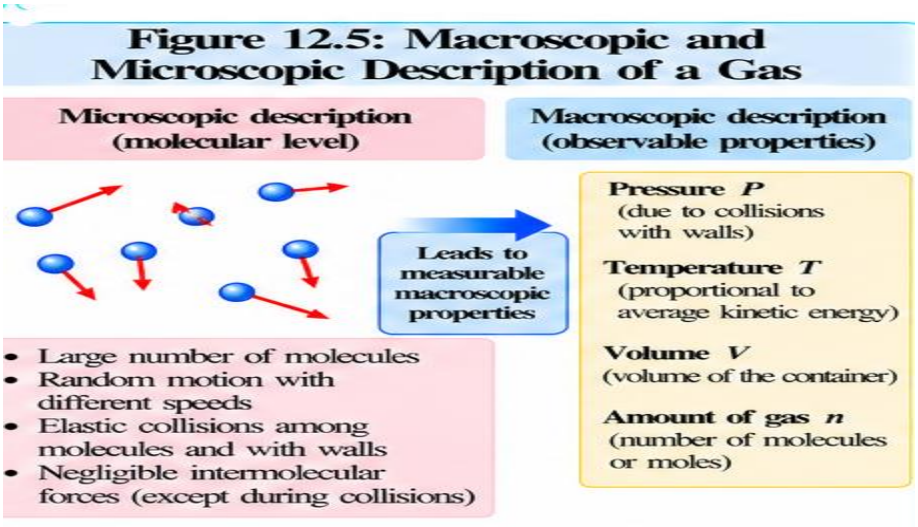


In the ideal gas model, gas molecules are point-like particles moving randomly, with no intermolecular forces except short-range forces during elastic collisions.

1.9 DIFFERENCE BETWEEN IDEAL GAS AND REAL GAS

Ideal Gas	Real Gas
A theoretical model.	A gas that exists physically.
Molecular volume is assumed negligible.	Molecules have finite size.
Intermolecular forces are neglected except during collisions.	Intermolecular forces are present.
Obeys PV= nRT exactly within the model.	Deviates from the ideal gas equation under some conditions.
Useful for simplifying kinetic-theory calculations.	May require more complex equations for accurate description.
Approximates the behaviour of many gases at low pressure and high temperature.	Deviations become important at high pressure and low temperature, particularly near condensation.

Important: Real gases generally behave more nearly ideally at low pressure and high temperature, provided they are sufficiently far from condensation.



1.10 SOLVED NUMERICAL EXAMPLES

Example 1: Calculation of Number of Molecules

Calculate the number of molecules present in 2 moles of an ideal gas.
Solution:
Given: n =2 mol, $N_A = 6.022 \times 10^{23}$
The number of molecules is:

$$N = nN_A = 2 \times 6.022 \times 10^{23} = 1.2004 \times 10^{24}$$

Example 2: Number of Moles

A gas sample contains 3.011×10^{23} molecules. Calculate the number of moles.
Solution:

$$\boldsymbol{n = \frac{N}{N_A} = \frac{3.011 \times 10^{23}}{6.022 \times 10^{23}} = 0.5}$$

Answer: 0.5 mole.

Example 3: Pressure of an Ideal Gas

Calculate the pressure exerted by 2 moles of an ideal gas occupying a volume of 0.05 m^3 at 300 K.
Solution
Given: n =2 mol V=0.05 m^3, T = 300 K, R = 8.314 J mol^{-1} K^{-1}
From the ideal gas equation:

$$PV = nRT$$

Therefore,

$$P = nRT/V = 2 \times 8.314 \times 300/0.05 = 9.98 \times 10^4 Pa$$

Try Yourself: Ideal Gas Equation in Molecular Form

A container contains 2.0×10^{23} molecules of an ideal gas at 300 K. The volume is 0.010 m^3..
Calculate the pressure.
Answer: The pressure is approximately 8.29×10^4 Pa.

1.11 IMPORTANT CONCEPTUAL QUESTIONS

Q1. Why does a gas exert pressure on the walls of its container?

Answer: Gas molecules collide continuously with the container walls and transfer momentum to them. The resulting force per unit area is the pressure.

Q2. Why is the average velocity of gas molecules zero at equilibrium?

Answer: Molecular motion is random and has no preferred direction. The velocity components cancel on average, giving zero average velocity in the rest frame of the gas.

Q3. Is the average speed of gas molecules zero?

Answer: No. Speed is a non-negative scalar quantity. Although the average velocity vector is zero at equilibrium, the average speed is positive.

Q4. Why is an ideal gas a useful model?

Answer: It simplifies the analysis of gas behaviour by neglecting molecular size and intermolecular forces, allowing the relationship between molecular motion and macroscopic properties to be studied.

Q5. What is the physical significance of Boltzmann's constant?

Answer: Boltzmann's constant connects temperature measured on a macroscopic scale with energy per particle on a microscopic scale.

Q6. What is the difference between R and k_B?

Answer: R is the universal gas constant used per mole, whereas k_B is Boltzmann's constant used per molecule.
Their relationship is: $R=N_A k_B$

PART 2: PRESSURE EXERTED BY AN IDEAL GAS, KINETIC THEORY EQUATION AND ROOT MEAN SQUARE SPEED

2.1 LEARNING OBJECTIVES

After studying this part, students will be able to:

1. Explain the microscopic origin of gas pressure.
2. Derive the expression for the pressure exerted by an ideal gas.
3. Understand the kinetic theory equation.
4. Relate gas pressure to the mean square speed of molecules.
5. Define mean square speed and root mean square speed.
6. Calculate the root mean square speed of gas molecules.
7. Explain the relationship between pressure, density and molecular speed.
8. Solve numerical problems based on kinetic theory.
9. Understand the assumptions and limitations of the kinetic theory model.

2.2 MOLECULAR ORIGIN OF GAS PRESSURE

A gas consists of a large number of molecules moving continuously and randomly in all directions.

When these molecules collide with the walls of their container, their momentum changes.

According to Newton's laws of motion, this change in momentum produces a force on the wall.

The force exerted by gas molecules per unit area of the container wall is called **gas pressure**.

$$\boxed{P = \frac{F}{A}}$$

Where:

- P = pressure
- F = normal force exerted on the wall
- A = area of the wall

The SI unit of pressure is the pascal (Pa).

$$\boxed{1\ pa = 1Nm^{-2}}$$

Important concept: Gas pressure is a macroscopic effect produced by the collective momentum transfer of a very large number of molecules.

2.3 DERIVATION OF THE KINETIC THEORY EQUATION

Consider an ideal gas enclosed in a cubical container.

Let: L = length of each side of the cube, V = volume of the container, N = total number of molecules, m = mass of each molecule, v_x = x-component of the velocity of a molecule, P = pressure exerted by the gas .

The volume of the cube is: $\boxed{V = L^3}$

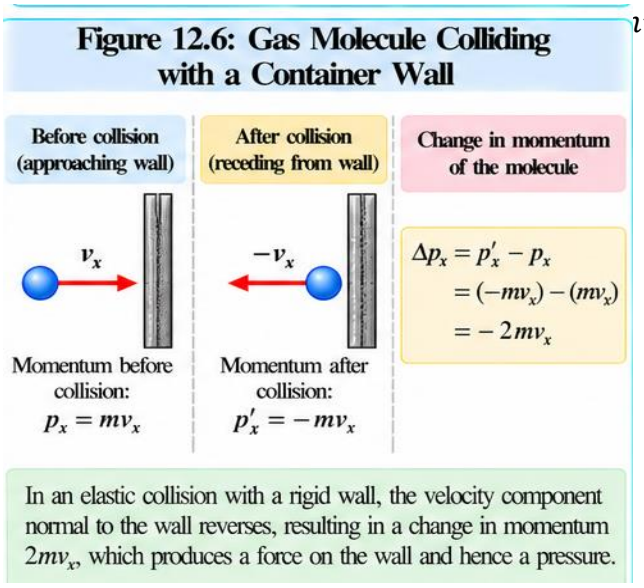
We assume that the molecules move randomly and collide elastically with the container walls.

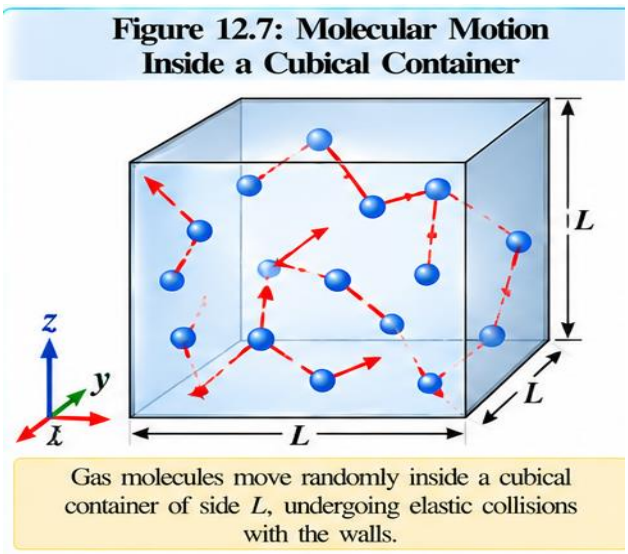
Change in Momentum during a Collision

Consider a molecule moving towards a wall perpendicular to the x-axis.

Let its velocity component perpendicular to the wall be v_x.

The change in momentum of the molecule is:





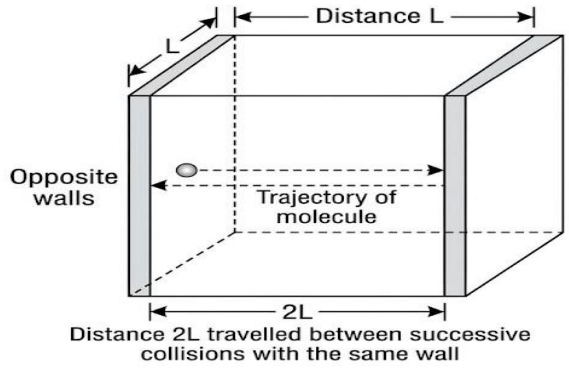


Figure 12.8: Derivation of Kinetic Theory of Gases

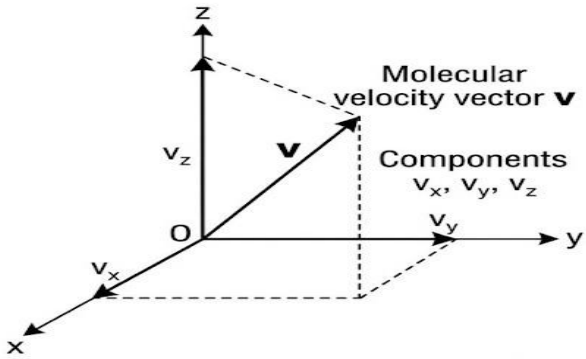


Figure 12.9: Velocity components of a Molecule

The magnitude of the momentum change is:

$$|\Delta p_x| = 2m|v_x|$$

By Newton's third law, the molecule transfers an equal and opposite momentum to the wall.
Therefore, the magnitude of momentum transferred to the wall in one collision is:

Time between Successive Collisions with the Same Wall

After colliding with one wall, the molecule travels to the opposite wall and returns before colliding with the original wall again. The total distance travelled in this interval is: 2 L
The time between successive collisions with the same wall is:

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

Average Force Exerted by One Molecule

Average force is the momentum transferred per unit time.
Therefore, the magnitude of the average force exerted by one molecule on the wall is:

$$F_1 = \frac{\Delta p_x}{\Delta t} = \frac{2m|v_x|}{2L/|v_x|} = \frac{m{v_x}^2}{L}$$

This is the average force contribution of one molecule to the wall perpendicular to the x-axis.

Total Force Exerted by N Molecules

For N molecules having different velocity components, the total average force on the wall is:

$$F = \frac{m[{v_{x1}}^2 + {v_{x2}}^2 + {v_{x3}}^2 + \ - - - - - -]}{L}$$

The pressure is force per unit area. Since the area of the wall is L^2.

$$P = \frac{F}{A} = \frac{F}{L^2} = \frac{mN[{v_{x1}}^2 + {v_{x2}}^2 + {v_{x3}}^2 + \ - - - - - -]}{NL^3}$$

$$P = mN\left(\frac{\overline{{v_x}^2}}{V}\right)$$

For a gas in equilibrium, molecular motion is isotropic, meaning that no direction is preferred. Thus,

$$\overline{{v_x}^2} = \overline{{v_y}^2} = \overline{{v_z}^2}$$

Since:

$$v^2 = {v_x}^2 + {v_y}^2 + {v_z}^2$$

Therefore,

$$\overline{v^2} = \overline{{v_x}^2} + \overline{{v_y}^2} + \overline{{v_z}^2} = 3\overline{{v_x}^2}$$

Or,

$$\overline{{v_x}^2} = \frac{\overline{v^2}}{3}$$

Substituting into the pressure equation: Pressure exerted on the wall by the gas is:

$$\boxed{P = \frac{1}{3}\left(\frac{mN}{V}\right)\left(\overline{v^2}\right)}$$

Or,

$$\boxed{P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m\overline{v^2}\right)}$$

This is the **kinetic theory equation of an ideal gas**.

2.4 IMPORTANT FORMS OF THE KINETIC THEORY EQUATION

The kinetic theory equation can be expressed in several useful forms.

2.4.1 In Terms of Number of Molecules

$$P = \frac{1}{3}\left(\frac{mN}{V}\right)\left(\overline{v^2}\right)$$

Where N is the number of molecules and m is the mass of each molecule.

2.4.2 In Terms of Gas Density

The density of the gas is:

$$\rho = \frac{mN}{V}$$

Therefore,

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

This is another important form of the kinetic theory equation.

Since:

$${v_{rms}}^2 = \overline{v^2}$$

We can write:

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

Or,

$$\boxed{v_{rms} = \sqrt{\frac{3P}{\rho}}}$$

This formula is useful when the pressure and density of a gas are known.

2.5 MEAN SQUARE SPEED

The **mean square speed** of gas molecules is the average of the squares of their individual speeds.

If the speeds of N molecules are $v_1, v_2, v_3, v_4, v_4, - - - - -$ then

$$\boxed{\overline{v^2} = \frac{{v_1}^2 + {v_2}^2 + {v_3}^2 + {v_4}^2 + - - - - -}{N}}$$

Alternatively,

$$\boxed{\overline{v^2} = \frac{1}{N}\sum_{i=1}^{n} {v_i}^2}$$

The SI unit of mean square speed is: $m^2 s^{-2}$

Important distinction:

Mean square speed is the average of the squares of speeds. It is not the square of the average speed.

In general:

$$\boxed{\overline{v^2} \neq \bar{v}^2}$$

2.6 ROOT MEAN SQUARE SPEED

The **root mean square speed**, abbreviated as RMS speed, is the square root of the mean square speed.

It is defined as:

$$\boxed{v_{rms} = \sqrt{\overline{v^2}}}$$

Therefore,

$$\boxed{v_{rms} = \sqrt{\frac{{v_1}^2 + {v_2}^2 + {v_3}^2 + - - - - - -}{N}}}$$

The SI unit of RMS speed is: $m\ s^{-1}$

RMS speed is particularly useful in kinetic theory because the pressure equation depends on the mean square speed.

2.6.1 Relation between Pressure, Density and RMS Speed

From the kinetic theory equation:

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

Therefore,

$$\boxed{v_{rms} = \sqrt{\frac{3P}{\rho}}}$$

This equation shows that RMS speed increases with pressure if the density remains constant.

2.7 DERIVATION OF RMS SPEED IN TERMS OF TEMPERATURE

The ideal gas equation is:

$$P = \frac{1}{3}\left(\frac{mN}{V}\right)\left(\overline{v^2}\right) - - - - - (1)$$

Or,

$$\overline{v^2} = {v_{rms}}^2 = \frac{3PV}{mN} = \frac{3nRT}{mN} - - - - (2)$$

Since Boltzmann's constant

$$k_B = \frac{R}{N_A} - - - - - (3)$$

Since, 1 mole has number of molecules equals to Avogadro's number (N_A).
Therefore, n moles has number of molecules,

$$N = nN_A - - - - - (4)$$

Using equations (2), (3) and (4), we get

$${v_{rms}}^2 = \frac{3nN_A k_B T}{mnN_A} = \frac{3k_B T}{m} - - - - (5)$$

Hence, we obtain

$$\boxed{v_{rms} = \sqrt{\frac{3k_B T}{m}}}$$

This expression gives the RMS speed in terms of the temperature and mass of an individual molecule.

Important Conclusions

From:

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

We obtain the following results:

1. RMS speed is proportional to the square root of absolute temperature $\left(v_{rms} \propto \sqrt{T}\right)$
2. RMS speed is inversely proportional to the square root of molecular mass $\left(v_{rms} \propto 1/\sqrt{m}\right)$
3. At the same temperature, lighter molecules have greater RMS speeds than heavier molecules.
4. If the absolute temperature becomes four times its initial value, the RMS speed becomes twice its initial value.

2.8 RMS SPEED IN TERMS OF MOLAR MASS

The RMS speed can also be expressed using the molar mass of the gas.
We know:

$$P = \frac{1}{3}\left(\frac{mN}{V}\right)\left(\overline{v^2}\right)$$

Or,

$$\overline{v^2} = {v_{rms}}^2 = \frac{3PV}{mN} = \frac{3nRT}{mN}$$

Since, 1 molecule has mass m, so, N molecules will have total mass = mN= m'
Now,

$$n = \frac{Total\ mass}{Molar\ mass} = \frac{m'}{M} = \frac{mN}{M}$$

Or,

$$\frac{mN}{n} = M$$

Therefore,

$${v_{rms}}^2 = \frac{3RT}{M}$$

Or

$$\boxed{v_{rms} = \sqrt{\frac{3RT}{M}}}$$

Where:

- R = universal gas constant
- T = absolute temperature in kelvin
- M = molar mass in kg mol^{-1}

Important unit rule: When using R= 8.314 J $mol^{-1}K^{-1}$}, express the molar mass in kg mol^{-1} to obtain RMS speed in m s^{-1}.
For example: $M(O_2)$ = 32 g mol^{-1} =0.032 kg = 0.032 kg mol^{-1}

2.9 SOLVED NUMERICAL EXAMPLES

Example 1: RMS Speed of Oxygen Molecules
Calculate the RMS speed of oxygen molecules at 300 K.
Given: T=300 K, R= 8.314 J mol^{-1} K^{-1}, M=0.032 kg mol^{-1}
The RMS speed is:

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 300}{0.032}} \approx 484 m/s$$

Answer: The RMS speed of oxygen molecules at 300 K is approximately 484 m s^{-1}.

Example 2: RMS Speed of Hydrogen Molecules
Calculate the RMS speed of hydrogen molecules at 300 K.
Given: T=300 K, R= 8.314 J mol^{-1} K^{-1}, M=0.002 kg mol^{-1}

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 300}{0.002}} \approx 1.93 \times 10^3 m/s$$

Answer: The RMS speed of hydrogen molecules is approximately 1.93 × 10^3 m s^{-1}.

Conceptual conclusion: Hydrogen molecules have a greater RMS speed than oxygen molecules at the same temperature because hydrogen has a much smaller molar mass.

Example 3: RMS Speed at Different Temperatures

The RMS speed of a gas is 400 m s^{-1} at 300 K. Calculate its RMS speed at 1200 K, assuming the gas remains ideal.

Given: $v_{rms1} = 400\ m/s, T_1 = 300\ K, T_2 = 1200\ K, v_{rms2} = ?$

Since,

$$\boldsymbol{v_{rms} \propto \sqrt{T}}$$

Therefore,

$$\boldsymbol{\frac{v_{rms1}}{v_{rms2}} = \sqrt{\frac{T_1}{T_2}} \Rightarrow v_{rms2} = \sqrt{\frac{T_2}{T_1}} \times v_{rms1} = \sqrt{\frac{1200}{300}} \times 400 = 800}$$

Answer: The RMS speed becomes 800 m s^{-1}.

Example 4: RMS Speed from Pressure and Density

A gas has a pressure of 1.0×10^5 Pa and a density of 1.25 kg m^{-3}. Calculate its RMS speed.

Given: $P = 1 \times 10^5 Pa, \rho = 1.25\ (= \frac{5}{4})\ kgm^{-3}, v_{rms} = ?$

We know that

$$\boldsymbol{v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \times 1 \times 10^5}{5/4}} = 2 \times 10^2\sqrt{6} \approx 490}$$

Answer: The RMS speed is approximately 490 m s^{-1}.

Example 5: Mean Square Speed

The RMS speed of a gas is 500 m s^{-1}. Calculate its mean square speed.

Given: $v_{rms} = 500\ m/s$

Since, $\overline{v^2} = {v_{rms}}^2 = 500 \times 500 = 250000$

Answer: The mean square speed is 2.5×10^5 m^2 s^{-2}.

2.10 IMPORTANT CONCEPTUAL QUESTIONS

Q1. Why is the RMS speed used in kinetic theory instead of average velocity?

Answer: Average velocity is zero for a gas in equilibrium because molecular velocities cancel in different directions. RMS speed is positive and is related directly to the mean square speed appearing in the pressure equation.

Q2. What is the physical meaning of the kinetic theory equation?

Answer: It shows that gas pressure is related to molecular mass, number density and the mean square speed of the molecules.

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

Q3. How does RMS speed change when the absolute temperature is increased fourfold?

Answer: RMS speed is proportional to the square root of absolute temperature. Therefore, if temperature becomes four times its initial value, RMS speed becomes twice its initial value.

Q4. Which gas has a greater RMS speed at the same temperature: hydrogen or oxygen?

Answer: Hydrogen has a greater RMS speed because its molar mass is smaller.

Q5. What is the relationship between pressure and RMS speed when gas density remains constant?

Answer:

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

For constant density:

$$P \propto {v_{rms}}^2$$

Q6. What happens to the RMS speed of a gas when its temperature approaches absolute zero according to the classical ideal-gas model?

Answer: The classical expression predicts that RMS speed approaches zero as absolute temperature approaches zero. Real gases may undergo condensation or other phase changes before this limit is reached, so the classical ideal-gas model is not generally valid all the way to absolute zero.

PART 3: KINETIC ENERGY AND TEMPERATURE, DEGREES OF FREEDOM, LAW OF EQUIPARTITION OF ENERGY AND SPECIFIC HEAT CAPACITIES

3.1 LEARNING OBJECTIVES

After studying this part, students will be able to:

1. Establish the relationship between the absolute temperature and the average translational kinetic energy of gas molecules.
2. Calculate the average kinetic energy of a molecule at a given temperature.
3. Understand the concept of degrees of freedom.
4. Distinguish between translational, rotational and vibrational degrees of freedom.
5. State and apply the law of Equipartition of energy.
6. Calculate the internal energy of an ideal gas.
7. Derive the expressions for the molar specific heat capacities of ideal gases.
8. Explain Mayer's relation.
9. Calculate the ratio of specific heat capacities, γ.
10. Solve numerical problems based on kinetic theory and specific heat capacities.

3.2 RELATION BETWEEN TEMPERATURE AND MOLECULAR KINETIC ENERGY

Temperature is one of the most important macroscopic properties of a gas. According to kinetic theory, it is directly related to the average translational kinetic energy of its molecules.
In Part 2, we derived the kinetic theory equation:

$$P = \frac{1}{3}\left(\frac{mN}{V}\right)(\overline{v^2})$$

Therefore,

$$PV = \frac{1}{3}(mN)({v_{rms}}^2)$$

For an ideal gas, the equation of state is:

$$PV = Nk_BT$$

Equating these two expressions:

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

Cancelling N:

$$\frac{1}{3}m{v_{rms}}^2 = k_BT$$

Multiplying both sides by 3 and dividing by 2:

$$\frac{1}{2}m{v_{rms}}^2 = \frac{3}{2}k_BT$$

The mean translational kinetic energy of a molecule is:

$$K_{trans} = \frac{1}{2}m{v_{rms}}^2$$

Hence,

$$\boxed{\boldsymbol{K_{trans} = \frac{3}{2}k_BT}}$$

This is a fundamental result of the kinetic theory of gases.

3.2.1 Important Conclusions

The average translational kinetic energy of a gas molecule:

1. Is directly proportional to its absolute temperature.
2. Depends only on temperature for an ideal gas.
3. Is independent of the molecular mass at a given temperature
4. Is the same for different ideal gases at the same temperature

Thus, at the same temperature, the average translational kinetic energy of a hydrogen molecule and an oxygen molecule is equal, although their RMS speeds are different.

Important distinction: Equal average translational kinetic energies do not imply equal molecular speeds. Lighter molecules move faster on average than heavier molecules at the same temperature.

3.3 AVERAGE TRANSLATIONAL KINETIC ENERGY PER MOLE

For one molecule:

$$\boxed{(K_{trans})_{molecule} = \frac{3}{2}k_B T}$$

For one mole of an ideal gas, the number of molecules is N_A

Therefore, the total translational kinetic energy per mole is:

$$K_{trans} = \frac{3}{2}N_A k_B T$$

Since:

$$R = N_A k_B$$

We obtain:

$$\boxed{(K_{trans})_{mole} = \frac{3}{2}RT}$$

For n moles of an ideal gas:

$$\boxed{(K_{trans})_{total} = \frac{3}{2}nRT}$$

This expression gives the total translational kinetic energy of n moles of an ideal gas.

Important Note

The expression $(3/2)nRT$ represents the translational kinetic energy of an ideal gas. For a gas with rotational and vibrational energy contributions, the total internal energy may be greater.

3.4 SOLVED EXAMPLES: KINETIC ENERGY AND TEMPERATURE

Example 1: Average Kinetic Energy of a Molecule

Calculate the average translational kinetic energy of a gas molecule at 300 K.

Given: T=300 K, 1.38×10^{-23} J K^{-1}

Using: $\overline{K}_{trans} = \frac{3}{2}k_B T = \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 = 6.21 \times 10^{-21} J$

Answer: The average translational kinetic energy is approximately 6.21×10^{-21} J per molecule.

Example 2: Average Kinetic Energy at 600 K

Calculate the average translational kinetic energy of a gas molecule at 600 K.

Given: T= 600 K, $k_B = 1.381 \times 10^{-23}$ J K^{-1}

Using: $\bar{K}_{trans} = 3/2\ k_B\ T = 3/2 \times 1.38 \times 10^{-23} \times 600 = 12.42 \times 10^{-21})$ J
Answer: The average translational kinetic energy at 600 K is twice its value at 300 K.

Example 3: Total Translational Kinetic Energy

Calculate the total translational kinetic energy of 2 moles of an ideal gas at 300 K.
Given: n = 2 mol, T = 300 K, R = 8.314 J mol^{-1} K^{-1}
Using:

$$(K_{trans})_{totl} = \frac{3}{2}nRT = \frac{3}{2} \times 8.314 \times 300 = 7.48\ kJ$$

Answer: The total translational kinetic energy is approximately 7.48 kJ.

3.5 Degrees of Freedom & Law of Equipartition of Energy

3.5.1 Introduction

Gas molecules possess different types of motion. Each independent mode of motion in which a molecule can store energy is called a **Degree of Freedom**.
The concept of degrees of freedom is essential for understanding:

- Internal Energy
- Specific Heat Capacities
- Equipartition of Energy
- Thermodynamics

3.5.2 Degree of Freedom (f)

Definition

A **Degree of Freedom** is an independent way in which a molecule can possess or store energy.
It is represented by the symbol: f

3.5.3 Types of Degrees of Freedom

A molecule may have three types of motion:

(i) Translational Motion

Movement along the three mutually perpendicular axes:

- x-axis
- y-axis
- z-axis

Hence,

$$\boxed{3\ Translational\ Degree\ of\ Freedom}$$

(ii) Rotational Motion

Rotation about the molecular axes
The number of rotational degrees depends on the type of molecule.

(iii) Vibrational Motion

Atoms within a molecule vibrate about their mean positions.
At ordinary temperatures, vibrational degrees of freedom are often negligible for simple gases.

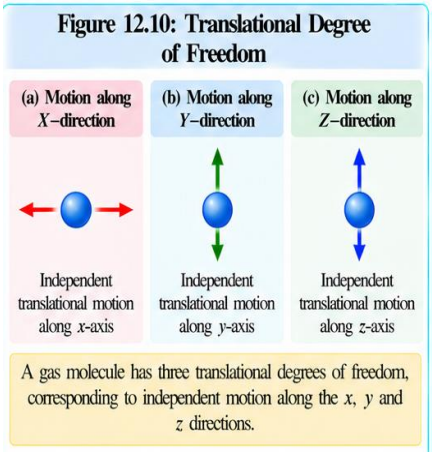


Figure 12.10: Translational Degree of Freedom

A gas molecule has three translational degrees of freedom, corresponding to independent motion along the x, y and z directions.

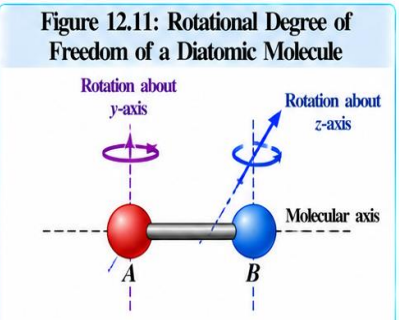


Figure 12.11: Rotational Degree of Freedom of a Diatomic Molecule

A diatomic molecule has two rotational degrees of freedom, corresponding to rotation about two mutually perpendicular axes (y and z) passing through the centre of mass and perpendicular to the molecular axis.

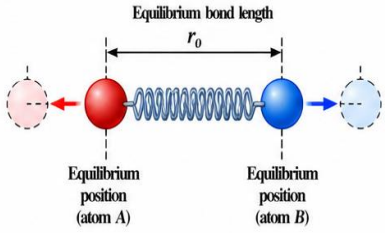


Figure 12.12: Vibrational Motion of a Diatomic Molecule

In vibrational motion, the two atoms oscillate about their equilibrium positions along the molecular axis, with periodic change in the bond length r around the equilibrium value r_0.

3.5.4 Degrees of Freedom of Different Gases

(A) Monoatomic Gas

Examples:

- Helium (He)
- Neon (Ne)
- Argon (Ar)

Only translational motion is possible.

$$\boxed{f = 3}$$

(B) Diatomic Gas

Examples:

- Hydrogen (H_2)
- Nitrogen (N_2)
- Oxygen (O_2)

At ordinary temperature:

- 3 Translational
- 2 Rotational

$$\boxed{f = 5}$$

At very high temperatures, vibrational motion becomes active:

$$\boxed{f = 7}$$

(C) Polyatomic Gas

Examples:

- Carbon dioxide (CO_2)
  At ordinary temperatures for CO_2 (Linear polyatomic gas)
  $$\boxed{f = 5}$$
- Methane (CH_4)
  At ordinary temperatures for CH_4 (Non-linear polyatomic gas)
  $$\boxed{f = 6}$$

3.5.5 Summary Table

Gas	Degrees of Freedom (ff)
Monoatomic	3
Diatomic (Ordinary Temperature)	5
Diatomic (High Temperature)	7 (This value assumes that the vibrational mode is fully active in the classical equipartition approximation.)
Non-linear polyatomic gas (ordinary-temperature approximation)	6

3.6 Law of Equipartition of Energy

Statement

The **Law of Equipartition of Energy** states:

At thermal equilibrium, energy is equally shared among all active degrees of freedom.

Each degree of freedom contributes:

$$\boxed{\frac{1}{2}k_BT}$$

per molecule.

3.7 Average Energy per Molecule

If a molecule has f degrees of freedom, then

$$\boxed{U = \frac{fk_BT}{2}}$$

Where:

- K_B = Boltzmann Constant
- T = Absolute Temperature

3.8 Average Energy per Mole

For one mole of gas,

$$N_Ak_B = R$$

Therefore,

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

Where:

- U = Internal Energy
- R = Universal Gas Constant

For n mole of a gas,

$$\boxed{U = \frac{nfRT}{2}}$$

3.9 Internal Energy of Different Gases

Monoatomic Gas

$$f = 3$$

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

Diatomic Gas

$$f = 5$$

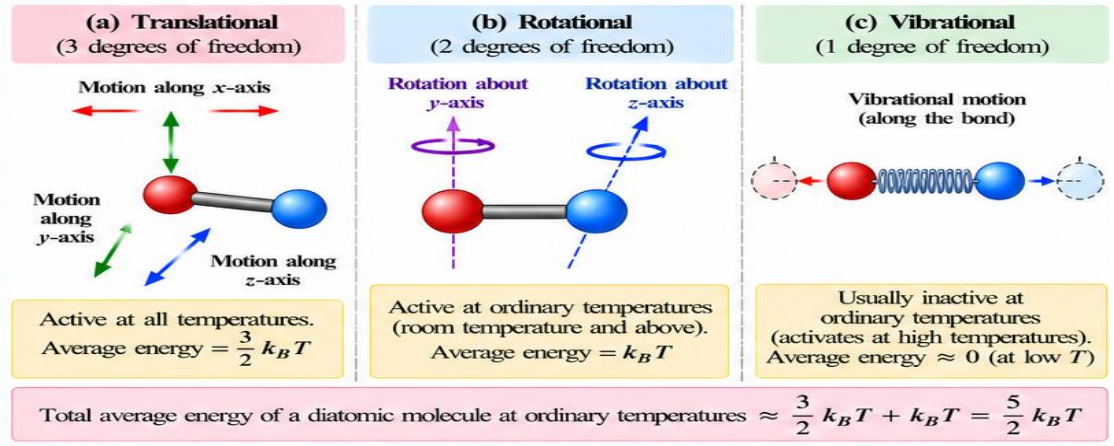
$$\boxed{U = \frac{5}{2}RT}$$

Polyatomic Gas

$$f = 6$$

$$\boxed{U = 3RT}$$

Figure 12.13: Energy Contributions in a Diatomic Molecule



3.10 Heat Capacities

From the Equipartition Theorem,

At Constant Volume

$$C_V = \frac{dU}{dt}$$

Therefore,

$$\boxed{C_V = \frac{fR}{2}}$$

At Constant Pressure

Using Mayer's Relation,

$$C_P = C_V + R$$

Hence,

$$\boxed{C_P = \left(\frac{f+2}{2}\right)R}$$

3.11 Ratio of Specific Heats

$$\boxed{\gamma = \frac{C_P}{C_V} = \frac{f+2}{f}}$$

3.12 Important Values

Gas	C_V	C_P	γ
Monoatomic	3R/2	5R/2	5/3
Diatomic	5R/2	7R/2	7/5
Polyatomic	3R	4R	4/3

3.13 In general, Heat capacity relation for an equation $PV^x = Constant$

$$C_m = C_V + \frac{R}{1-x}$$

Or,

$$C_m = \frac{R}{\gamma - 1} + \frac{R}{1-x}$$

For different thermodynamics processes, the value of C is as:

1) **Isobaric Process**

Pressure P = constant, hence, the equation of state is

$$PV^0 = Constant$$

Comparing this with equation,

$$PV^x = Constant$$

We get $x = 0$ and Molar heat capacity at constant pressure is

$$C_m = C_P = C_V + R$$

2) **Isochoric process**

Volume, V = Constant

Then the equation of state is

$$P^{1/\infty}V = Constant$$

Comparing this with general thermodynamics process,

$$PV^x + Constant \Rightarrow P^{1/x}V = Constant$$

We get $x = \infty$

Therefore, molar heat capacity at constant volume is

$$C_m = C_V = \frac{R}{\gamma - 1}$$

3) **Isothermal Process**

Temperature, T = constant,

The equation of state is

$$PV = Constant \Rightarrow PV^1 = Constant$$

Hence, we get $x = 1$ and molar heat capacity in Isothermal process is

$$C_m = C_V + \frac{R}{1-x} = C_V + \frac{R}{1-1} = \infty$$

Thus, $C_m = \infty$ in Isothermal process

4) Adiabatic Process

No heat is transferred, so, Q = 0

The equation of state is

$$PV^{\gamma} = Constant$$

Comparing this with general equation

$$PV^{x} = Constant$$

Hence, we get $x = \gamma$ and molar heat capacity in adiabatic process is

$$C_m = \frac{R}{\gamma - 1} + \frac{R}{1 - x} = \frac{R}{\gamma - 1} + \frac{R}{1 - \gamma} = 0$$

Thus, molar heat capacity in Adiabatic process is C = 0

Combining all these values of molar heat capacity for different thermodynamic processes in tabular form

Thermodynamics Process	Molar Heat Capacity (C)
Isobaric Process	$C_m = C_P = C_V + R$
Isochoric Process	$C_m = C_V = \frac{R}{\gamma} - 1$
Isothermal Process	$C_m = \infty$
Adiabatic Process	$C_m = 0$

3.14 Important Conceptual Questions

Q1. Why does a monoatomic gas have only three degrees of freedom?

Answer:

Because it behaves like a point particle and only translational motion is significant.

Q2. Why is C_P always greater than C_V?

Answer:

At constant pressure, a part of the supplied heat is used to perform external work during expansion.

Q3. Why does γ decrease as the degrees of freedom increase?

Answer:

Because additional degrees of freedom allow energy to be distributed among more modes, reducing the ratio C_P/C_V

3.15 SOLVED NUMERICAL EXAMPLES

Example 1: Internal Energy of a Monatomic Gas

Calculate the internal energy of 2 moles of a monatomic ideal gas at 300 K.

Given: n=2 mol, T=300 K, R=8.314 J mol^{-1} K^{-1}

By using:

$$U = \frac{nfRT}{2}$$

For a monatomic ideal gas: f = 3, Therefore,

$$U = \frac{3}{2}nRT = \frac{3}{2} \times 2 \times 8.314 \times 300 = 7.48\ kJ$$

Answer: The internal energy is approximately 7.48 kJ.

Example 2: Molar Heat Capacities of a Monatomic Gas
Calculate C_V and C_P for a monatomic ideal gas.
Given: R=8.314 J mol^{-1} K^{-1}
Since,

$$C_V = \frac{dU}{dT} = \frac{d}{dT}(nfRT/2) = \frac{nfR}{2} - - - -(1)$$

For a monatomic gas: f = 3, n = 1, therefore,

$$C_V = \frac{3 \times 8.314}{2} \approx 12.47\, Jmol^{-1}K^{-1}$$

And,

$$C_P = C_V + R = 12.47 + 8.341 \approx 20.79\, Jmol^{-1}K^{-1}$$

Answer:
CV≈12.47 J mol^{-1} K^{-1}
CP≈20.79 J mol^{-1} K^{-1}

Example 3: Change in Internal Energy
Three moles of a monatomic ideal gas are heated from 300 K to 400 K. Calculate the change in internal energy.
Given: n=3 mol, ΔT=400−300=100
Since,

$$\frac{dU}{dT} = \frac{d}{dT}(nfRT/2) = \frac{nfR}{2}$$

Or,

$$\Delta U = \frac{nfR}{2}\Delta T - - - -(1)$$

For a monatomic gas: f =3
Substituting the values in equation (1),

$$\Delta U = \frac{3 \times 3 \times 8.314 \times 100}{2} \approx 3.74\, kJ$$

Answer: The internal energy increases by approximately 3.74 kJ.

Example 4: Ratio of Specific Heats
Calculate the ratio of specific heats for a diatomic ideal gas at ordinary temperatures, neglecting vibrational modes.
Solution:
Specific heat ratio, γ and degree of freedom f is related as:

$$\gamma = 1 + \frac{2}{f}$$

For diatomic gas at ordinary temperature, f = 5
Therefore,

$$\gamma = 1 + \frac{2}{5} = 1.4$$

Answer: The ratio of specific heats is 1.4.

Example 5: Heat Supplied at Constant Volume
Two moles of a monatomic ideal gas are heated at constant volume through 50 K. Calculate the heat supplied.
Solution:
Given: n=2 mol, ΔT=50 K
At constant volume, $W = PdV = 0$; for monoatomic gas: $C_V = 3R/2$
Therefore,

$$Q = \Delta U = nC_V\Delta T = 2 \times \frac{3R}{2} \times 50 = 150 \times 8.314 \approx 1.25kJ$$

Answer: Approximately 1.25 kJ of heat is supplied.

Example 6: Heat Supplied at Constant Pressure
One mole of a monatomic ideal gas is heated at constant pressure through 100 K. Calculate the heat supplied.
Solution
Given: n=1 mol, ΔT=100 K; $C_P = 5R/2$ for monoatomic gas

$$Q = nC_P\Delta T = 1 \times \frac{5R}{2} \times 100 = 250 \times 8.314 \approx 2.08\ kJ$$

Answer: Approximately 2.08 kJ of heat is supplied.

3.16 IMPORTANT CONCEPTUAL QUESTIONS

Q1. What is the relationship between the absolute temperature and average translational kinetic energy of a gas molecule?

Answer:

$$\overline{K}_{translational} = \frac{3}{2}k_BT$$

The average translational kinetic energy is directly proportional to the absolute temperature.

Q2. Do hydrogen and oxygen molecules have the same average translational kinetic energy at the same temperature?

Answer: Yes. For ideal gases at the same temperature, the average translational kinetic energy per molecule is the same, irrespective of molecular mass.

Q3. Why does a hydrogen molecule have a greater RMS speed than an oxygen molecule at the same temperature?

Answer: RMS speed is inversely proportional to the square root of molecular mass. Since hydrogen molecules are much lighter than oxygen molecules, their RMS speed is greater.

Q4. What is meant by degrees of freedom?

Answer: Degrees of freedom are the number of independent coordinates or active independent modes required to describe the motion and energy of a system under a specified model.

Q5. State the law of equipartition of energy.

Answer: In classical thermal equilibrium, each independent quadratic term in the energy contributes an average energy of $1(1/2)k_BT$ per molecule.

Q6. Why is the molar heat capacity at constant pressure greater than that at constant volume?

Answer: At constant volume, no expansion work is done. At constant pressure, some of the heat supplied is used to perform expansion work. Therefore, more heat is required to raise the temperature of one mole by the same amount at constant pressure.

Q7. State Mayer's relation.

Answer: For an ideal gas: $C_P - C_V = R$

Q8. Why can the specific heat capacities of a real gas vary with temperature?

Answer: Different molecular energy modes may become active at different temperatures. In addition, real-gas interactions can affect its thermodynamic properties.

PART 4: MEAN SPEED, RMS SPEED, MOST PROBABLE SPEED AND MAXWELL'S DISTRIBUTION OF MOLECULAR SPEEDS

4.1 LEARNING OBJECTIVES

After studying this part, students will be able to:

1. Define mean speed, RMS speed and most probable speed.
2. Distinguish between the three characteristic molecular speeds.
3. Derive expressions for the three speeds using Maxwell's speed distribution.
4. Understand how molecular speed depends on temperature and molar mass.
5. Explain the shape and significance of the Maxwell speed distribution curve.
6. Understand how the speed distribution changes with temperature.
7. Solve numerical problems based on molecular speeds.
8. Apply the concepts to CBSE Board, NEET and JEE-level questions.

4.2 WHY DO GAS MOLECULES HAVE DIFFERENT SPEEDS?

Gas molecules are in continuous random motion. They collide with one another and exchange energy.

Even when a gas is in thermal equilibrium at a fixed temperature, all its molecules do not move at the same speed.

Some molecules move relatively slowly, some move at intermediate speeds, and some move very rapidly.

Therefore, a single speed cannot describe the motion of every molecule in a gas.

Instead, we use three important characteristic speeds:

1. **Most probable speed**
2. **Mean speed**
3. **Root mean square speed**

These quantities describe different aspects of the molecular speed distribution.

For an ideal gas at thermal equilibrium, the three speeds are related by:

$$\boxed{v_{mp} < v_{mean} < v_{rms}}$$

Where:

- v_{mp} = most probable speed
- v_{mean} = mean speed
- v_{rms} = root mean square speed

4.3 MOST PROBABLE SPEED

4.3.1 Definition

The **most probable speed** is the speed at which the Maxwell speed distribution curve reaches its maximum.

It is the speed associated with the highest probability density in the distribution.

It does not mean that every molecule, or even necessarily a majority of all molecules, has exactly this speed.

4.3.2 Formula for Most Probable Speed

For an ideal gas in thermal equilibrium, Maxwell's speed distribution gives:

$$\boxed{v_{mp} = \sqrt{\frac{2k_B T}{m}}}$$

Where:

- k_B = Boltzmann constant
- T = absolute temperature
- m = mass of one molecule

Using the relation between Boltzmann's constant and the universal gas constant:

$$R = N_A k_B$$

And the molar mass:

$$M = mN_A$$

We obtain:

$$v_{mp} = \sqrt{\frac{2RT}{M}}$$

Here, M must be expressed in kg mol^{-1} when R is used in SI units.

4.3.3 Dependence on Temperature

From:

$$v_{mp} = \sqrt{\frac{2RT}{M}}$$

For a fixed gas:

$$\boxed{v_{mp} \propto \sqrt{T}}$$

Thus, if the absolute temperature becomes four times its initial value, the most probable speed becomes twice its initial value.

4.3.4 Dependence on Molar Mass

For gases at the same temperature:

$$\boxed{v_{mp} \propto \frac{1}{\sqrt{M}}}$$

Therefore, lighter molecules have greater most probable speeds than heavier molecules at the same temperature.

4.4 MEAN SPEED

4.4.1 Definition

The **mean speed** is the arithmetic average of the speeds of all molecules in a gas sample.
If the speeds of N molecules are $v_1, v_2, v_3, --$, then:

$$\boxed{v_{mean} = \frac{v_1 + v_2 + v_3 + \ ---v_n}{N}}$$

Alternatively:

$$\boxed{v_{mean} = \frac{1}{N}\sum_{i=1}^{n} v_i}$$

Mean speed is a scalar quantity and is always non-negative.

It must not be confused with average velocity, which is a vector quantity.
For a gas in equilibrium, the average velocity vector is zero, but the mean speed is positive.

4.4.2 Formula for Mean Speed

According to Maxwell's speed distribution, the mean speed of an ideal gas is:

$$\boxed{v_{mean} = \sqrt{\frac{8k_BT}{\pi m}}}$$

In terms of molar mass:

$$\boxed{v_{mean} = \sqrt{\frac{8RT}{\pi M}}}$$

This formula gives the average speed of the molecules of an ideal gas at absolute temperature T.

4.4.3 Dependence on Temperature and Molar Mass

For a fixed gas:

$$\boxed{v_{mean} \propto \sqrt{T}}$$

For gases at the same temperature:

$$\boxed{v_{mean} \propto \frac{1}{\sqrt{M}}}$$

Thus, mean speed increases with temperature and decreases with increasing molecular mass.

4.5 ROOT MEAN SQUARE SPEED

4.5.1 Definition

The **root mean square speed**, or RMS speed, is the square root of the average of the squares of the molecular speeds.
For N molecules:

$$\boxed{v_{rms} = \sqrt{\frac{{v_1}^2 + {v_2}^2 + {v_3}^2 + ------ + {v_n}^2}{N}}}$$

Equivalently:

$$\boxed{v_{rms} = \sqrt{\overline{v^2}}}$$

4.5.2 Dependence on Temperature and Molar Mass

For a fixed gas:

$$v_{rms} \propto \sqrt{T}$$

For gases at the same temperature:

$$v_{rms} \propto \frac{1}{\sqrt{M}}$$

RMS speed is particularly important in kinetic theory because the pressure equation depends on the mean square speed:

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

4.6 COMPARISON OF THE THREE MOLECULAR SPEEDS

The three characteristic speeds of an ideal gas are:

Most probable speed

$$\boxed{v_{mp} = \sqrt{\frac{2RT}{M}}}$$

Mean speed

$$\boxed{v_{mean} = \sqrt{\frac{8RT}{\pi M}}}$$

RMS speed

$$\boxed{v_{rms} = \sqrt{\frac{3RT}{M}}}$$

Ratio of v_{rms} and v_{mp}

$$\boxed{\frac{v_{rms}}{v_{mp}} = \sqrt{\frac{3}{2}}}$$

Numerically,

$$\boxed{v_{rms} \approx 1.225 v_p}$$

Ratio of v_{mean} and v_{mp}

$$\boxed{\frac{v_{mean}}{v_{mp}} = \sqrt{\frac{4}{\pi}}}$$

Numerically,

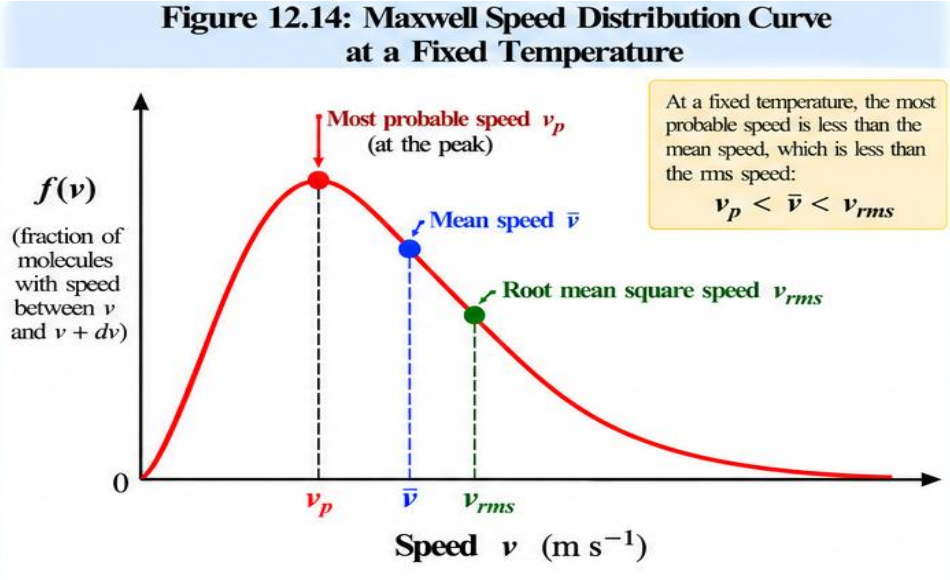
$$\boxed{v_{mean} \approx 1.128 v_{mp}}$$

Therefore, the order is:

$$\boxed{v_{mp} < v_{mean} < v_{rms}}$$

The ratio of the three speeds can also be written as:

$$\boxed{v_{mp} : v_{mean} : v_{rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}}$$



4.7 MAXWELL'S DISTRIBUTION OF MOLECULAR SPEEDS (NEET/JEE enrichment)

4.7.1 Introduction

The Maxwell speed distribution describes how the speeds of molecules in an ideal gas are distributed at thermal equilibrium.

The molecules do not all move at the same speed. Instead, their speeds follow a statistical distribution.

For an ideal gas at temperature T, the probability density of molecular speeds is described by the Maxwell distribution.

The distribution depends on:

- Absolute temperature T
- Molecular mass m
- Molecular speed v
- Boltzmann constant kBk_B

4.7.2 Maxwell Speed Distribution Formula

The probability density function for molecular speed is:

$$\boxed{f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{mv^2/2k_B T}}$$

Here:

- f(v) = probability density associated with speed v
- m = mass of one molecule
- T = absolute temperature
- k_B = Boltzmann constant
- v = molecular speed

The fraction of molecules with speeds between v and v+dv is:

$$\boxed{f(v)dv}$$

For a sample containing N molecules, the expected number of molecules in that speed interval is:

$$\boxed{dN = Nf(v)dv}$$

The function is normalized:

$$\boxed{\int_0^\infty f(v)dv = 1}$$

This means that the total fraction of molecules over all possible speeds is one.
Important: f(v) is a probability density, not the probability of finding a molecule at one exact speed. For a continuous distribution, the probability of an exact single speed is zero; probabilities are calculated over finite speed intervals.

4.8 CHARACTERISTICS OF THE MAXWELL DISTRIBUTION CURVE

The Maxwell speed distribution curve has the following features:

1. The horizontal axis represents molecular speed v.
2. The vertical axis represents the probability density f(v), or the number of molecules per unit speed interval when suitably scaled.
3. The curve begins at zero when v = 0.
4. It rises to a maximum at the most probable speed.
5. It then decreases gradually, forming a tail at high speeds.
6. The area under the curve represents the total fraction of molecules and equals one for a normalized distribution.
7. The mean speed and RMS speed lie to the right of the most probable speed.

The curve is not symmetric. It is positively skewed, meaning that its tail extends towards higher speeds.

Important Concept

The most probable speed corresponds to the maximum height of the curve, whereas the mean speed and RMS speed are calculated from averages over the entire distribution.

4.9 EFFECT OF TEMPERATURE ON THE MAXWELL DISTRIBUTION

Consider the same ideal gas at two temperatures, T_1 and T_2, where: $T_2 > T_1$
When the temperature increases:

1. The characteristic molecular speeds increase.
2. The most probable speed shifts to the right.
3. The mean speed increases.
4. The RMS speed increases.
5. The distribution curve generally becomes broader.
6. Its peak becomes lower.
7. The total area under the normalized distribution remains equal to one.

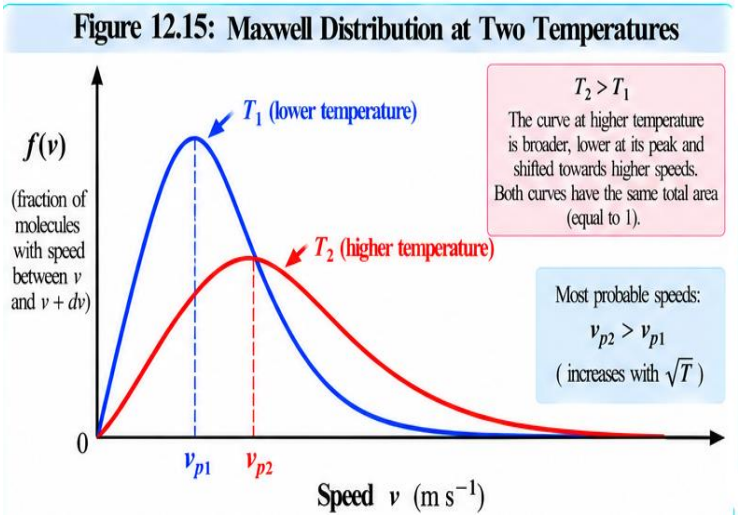
The increase in characteristic speeds follows:

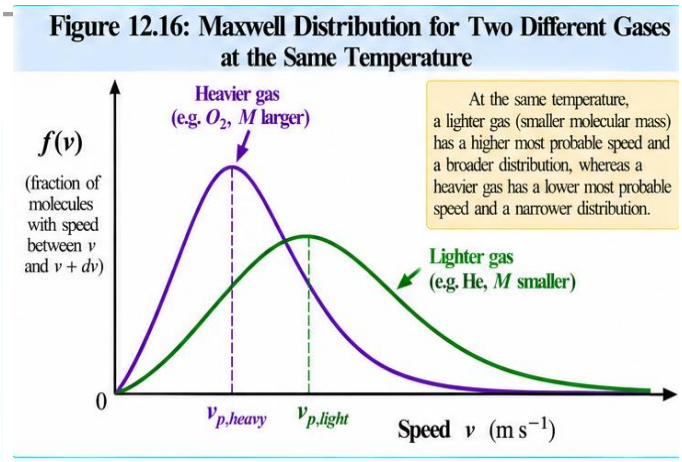
$$v_{mp} \propto \sqrt{T}$$

$$v_{mean} \propto \sqrt{T}$$

$$v_{rms} \propto \sqrt{T}$$

Thus, increasing temperature does not make all molecules move at one new speed. It changes the entire distribution of molecular speeds.





4.10 EFFECT OF MOLECULAR MASS ON THE DISTRIBUTION

Consider two different ideal gases at the same temperature.
Let their molecular masses be m_1 and m_2, with: $m_1 < m_2$
Their RMS speeds satisfy:

$$v_{rms} = \sqrt{\frac{3k_BT}{m}}$$

Therefore,

$$\boxed{\frac{v_{rms,1}}{v_{rms,2}} = \sqrt{\frac{m_2}{m_1}}}$$

The lighter gas has greater characteristic molecular speeds.
Similarly:

$$\boxed{\frac{v_{mp,1}}{v_{mp,2}} = \sqrt{\frac{m_2}{m_1}}}$$

And

$$\boxed{\frac{v_{mean,1}}{v_{mean,2}} = \sqrt{\frac{m_2}{m_1}}}$$

For the same temperature, the average translational kinetic energy per molecule is the same for all ideal gases, although their characteristic speeds differ.
Important: Different gases at the same temperature have the same average translational kinetic energy per molecule, but their characteristic speeds differ because their molecular masses differ.

4.11 SOLVED NUMERICAL EXAMPLES

Example 1: Most Probable Speed of Oxygen
Calculate the most probable speed of oxygen molecules at 300 K.

Given: T=300 K, R=8.314 J $mol^{-1}K^{-1}$, M=0.032 kg mol^{-1}
The most probable speed is:

$$v_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314 \times 300}{0.032}} \approx 395\ m/s$$

Answer: The most probable speed is approximately 395 m s^{-1}.

Example 2: Mean Speed of Oxygen
Calculate the mean speed of oxygen molecules at 300 K.
Given: T=300 K, R=8.314 J $mol^{-1}K^{-1}$, M=0.032 kg mol^{-1}
The mean speed is:

$$v_{mean} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 300}{3.14 \times 0.032}} \approx 446\ m/s$$

Answer: The mean speed is approximately 446 m s^{-1}.

Example 3: RMS Speed of Oxygen
Calculate the RMS speed of oxygen molecules at 300 K.
Given: T=300 K, R=8.314 J $mol^{-1}K^{-1}$, M=0.032 kg mol^{-1}
Using:

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 300}{0.032}} \approx 484\ m/s$$

Answer: The RMS speed is approximately 484 m s^{-1}.

Comparison

For oxygen at 300 K:

$$v_{mp} \approx 395\frac{m}{s};\ v_{mean} \approx 446\frac{m}{s};\ v_{rms} \approx 484\ m/s$$

Example 4: Ratio of RMS Speeds of Hydrogen and Oxygen
Calculate the ratio of RMS speeds of hydrogen and oxygen molecules at the same temperature.
Given: M_{H2} =2 g mol^{-1}, M_{O2} =32 g mol^{-1}
For gases at the same temperature:

$$v_{rms} \propto \frac{1}{\sqrt{M}}$$

Therefore,

$$\frac{v_{rms,H}}{v_{rms,O}} = \sqrt{\frac{M_{2,O}}{M_{1,O}}} = \sqrt{\frac{32}{2}} = 4$$

Answer: The RMS speed of hydrogen molecules is four times that of oxygen molecules at the same temperature.
The same ratio applies to their mean speeds and most probable speeds.

Example 5: Change in RMS Speed with Temperature
The RMS speed of a gas is 400 m s^{-1} at 300 K. Find its RMS speed at 1200 K.
Given: v_1 = 400 m s^{-1}, T_1=300 K, T_2 =1200 K

For the same gas:

$$v_{rms} \propto \sqrt{T}$$

Therefore,

$$\frac{v_{1,rms}}{v_{2,rms}} = \sqrt{\frac{T_1}{T_2}} = \sqrt{\frac{300}{1200}} = \sqrt{\frac{1}{4}} = \frac{1}{2}$$

Hence,

$$v_{2,rms} = 2 \times v_{1,rms} = 2 \times 400 = 800\ m/s$$

Answer: The RMS speed becomes 800 m s^{-1}.

4.12 IMPORTANT CONCEPTUAL QUESTIONS

Q1. Why do molecules of a gas have different speeds at the same temperature?

Answer: Molecules continuously collide and exchange energy. At thermal equilibrium, their speeds follow a statistical distribution rather than having one common value.

Q2. Which is greater: mean speed or RMS speed?

Answer: RMS speed is greater than mean speed for a Maxwell-distributed ideal gas:

$$v_{rms} > v_{mean} > v_{mp}$$

Q3. What does the most probable speed represent?

Answer: It is the speed at which the Maxwell speed distribution curve reaches its maximum.

Q4. Does the most probable speed represent the speed of every molecule?

Answer: No. It is the speed associated with the maximum probability density. Molecules have a range of speeds.

Q5. What happens to the Maxwell distribution curve when temperature increases?

Answer: The curve broadens, its peak becomes lower, and its characteristic speeds shift towards higher values. The total area under a normalized curve remains one.

Q6. Why do lighter molecules have greater RMS speeds at the same temperature?

Answer: Since:

$$v_{rms} = \sqrt{\frac{3k_BT}{m}}$$

RMS speed is inversely proportional to the square root of molecular mass.

Q7. Are the average translational kinetic energies of hydrogen and oxygen molecules equal at the same temperature?

Answer: Yes. For an ideal gas:

$$\bar{K}_{trans} = \frac{3}{2}k_BT$$

The average translational kinetic energy per molecule depends only on temperature, not molecular mass.

Part–5: Mean Free Path, Collision Frequency, Real Gases & Limitations

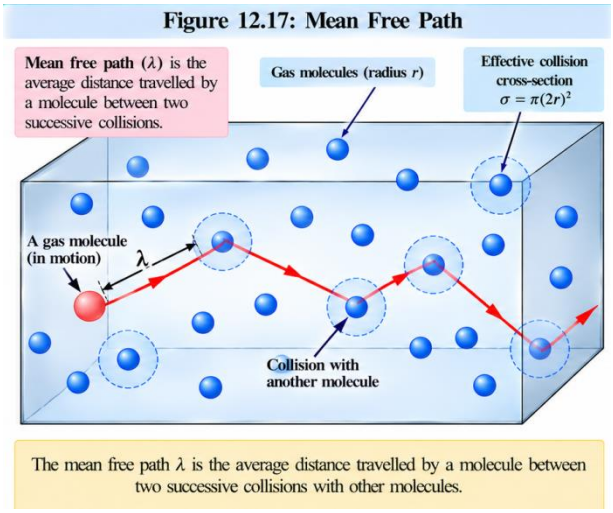
5.1 Mean Free Path (λ)

Definition

The **Mean Free Path** is the **average distance travelled by a gas molecule between two successive collisions**.

It is denoted by: λ

SI Unit: metre (m)



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

λ = mean free path
d = diameter of a gas molecule
n = number of molecules per unit volume

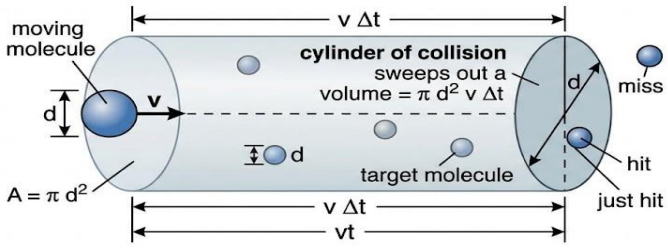


Figure 12.18: Derivation of Mean Free Path

5.2 Expression for Mean Free Path

For an ideal gas,

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

Where,

- λ = Mean free path
- d = Diameter of a gas molecule
- n = Number of molecules per unit volume (number density) or number density

5.3 Dependence of Mean Free Path

From the above expression:

(i) Effect of Pressure

As pressure increases,

- Number density increases.
- Mean free path decreases.

$$\boxed{\lambda \propto \frac{1}{P}}$$

(at constant temperature)

(ii) Effect of Temperature

At constant pressure,
an increase in temperature generally increases the mean free path because the gas expands and the number density decreases.

(iii) Effect of Molecular Size

Larger molecular diameter means more frequent collisions.
Hence,

$$\boxed{\lambda \propto \frac{1}{d^2}}$$

5.4 Collision Frequency

Definition

The **Collision Frequency** is the **number of collisions made by a molecule per second**.
It is denoted by: Z
SI Unit: s^{-1}

5.5 Relation Between Mean Free Path and Collision Frequency

If v_{avg} is the average speed,

$$\boxed{Z = \frac{v_{avg}}{\lambda}}$$

Hence,

- Larger mean free path → Lower collision frequency.
- Smaller mean free path → Higher collision frequency.

5.6 Real Gases and Ideal Gases

Ideal Gas

An ideal gas is a hypothetical gas that satisfies:

$$PV = nRT$$

under all conditions.
Assumptions:

- No intermolecular forces.
- Negligible molecular volume.
- Perfectly elastic collisions.

Real Gas

A real gas:

- Has finite molecular size.
- Experiences intermolecular forces.
- Deviates from ideal behaviour at **high pressure** and **low temperature**.

Examples:

- Oxygen
- Nitrogen
- Carbon dioxide
- Hydrogen

5.7 Conditions for Ideal Behaviour of Real Gases

A real gas behaves approximately like an ideal gas when:

- Pressure is **low**.
- Temperature is **high**.

Reason:

- Molecules remain far apart.
- Intermolecular forces become negligible.

5.8 Limitations of the Kinetic Theory

The kinetic theory is based on ideal assumptions and has the following limitations:

(i)

It assumes that molecules are point particles.
In reality, molecules have finite size.

(ii)

It neglects intermolecular forces.
Real gases always possess attractive and repulsive forces.

(iii)

The simple kinetic theory model assumes perfectly elastic collisions. In real molecular interactions, translational kinetic energy may be exchanged with internal molecular energy, although total energy is conserved..

(iv)

It cannot accurately explain the behaviour of gases near liquefaction.

(v)

It fails at very high pressures and very low temperatures.

5.9 Successes of the Kinetic Theory

The theory successfully explains:

- Boyle's Law
- Charles's Law
- Avogadro's Law

- Gas pressure
- Internal energy
- RMS speed
- Temperature as a measure of molecular kinetic energy

5.10 Boyle's Law from Kinetic Theory

At constant temperature,
Average kinetic energy remains constant.
Hence,

$$\overline{v^2} = Constant$$

Using

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

And

$$\rho = \frac{m}{V}$$

We obtain:

$$\boxed{PV = Constant}$$

Thus, Boyle's Law is explained.

5.11 Charles's Law from Kinetic Theory

From

$$\overline{KE} = \frac{3}{2}k_B T$$

As temperature increases,

- Molecular kinetic energy increases.
- Molecular speed increases.
- At constant pressure, the gas expands.

Therefore,

$$\boxed{V \propto T}$$

5.12 Important Conceptual Questions

Q1. Why does the mean free path decrease with increasing pressure?
Answer:
Because molecules come closer together, resulting in more frequent collisions.

Q2. Why do real gases deviate from ideal behaviour at high pressure?
Answer:
At high pressure, molecules are very close, so their finite size and intermolecular forces become significant.

Q3. Why does a real gas behave ideally at high temperature?
Answer:
At high temperatures, the kinetic energy of molecules is much greater than the intermolecular attractive forces.