

Kinetic theory of gas explains the behaviour of gases based on the idea that the gas consists of rapidly moving atoms or molecules. Interatomic forces which are short range forces can be neglected in gases, this explains the rapid movement of gases.

KINETIC THEORY

|TOPIC 1|

Behaviour and Kinetic Interpretation of Gases

MOLECULAR NATURE OF MATTER

In 20th century, **Richard Feynman**, one of the great physicists discovered that matter is made up of atoms.

The scientific atomic theory is usually credited to **John Dalton** (1766-1844), an English chemist. He proposed the atomic theory to explain the laws of definite and multiple proportions obeyed by elements when they combine into compounds.

- (i) Law of definite proportion states that any given compound has a fixed proportion by mass of its constituents.
- (ii) Law of multiple proportion states that when two elements combined to form more than one compound, for a fixed mass of one element, the masses of other elements are in ratio of small integers.

About 200 years ago, John Dalton suggested that 'the smallest constituents of an element are atoms. Atoms of one element are identical but differ from those of other elements. A small number of atoms of each element combine to form a molecule of the compound.'

As number of atoms combine to form a molecule so Dalton's atomic theory is also referred as molecular theory of matter.

In 19th century, Gay Lussac stated that

'when gases combine chemically to yield another gas, their volumes are in the ratio of small integers.'



CHAPTER CHECKLIST

- Molecular Nature of Matter
- Behaviour of Gases
- Law for an Ideal Gas
- Kinetic Theory of Ideal Gas
- Degree of Freedom
- Law of Equipartition of Energy
- Specific Heat Capacity
- Mean Free Path
- Brownian Motion

Amedeo Avogadro (1776-1856) helped to understand the combination of different gases in a simple manner. Avogadro's law says that,

equal volumes of all gases at the same temperature and pressure have equal number of molecules when Avogadro's law combined with Dalton's theory to explain Gay Lussac's law.

Atomic Hypothesis

All things are made of atoms. The atoms are little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. Advancement in science and technology enable us to see the molecules with the help of electron microscope and scanning tunneling microscope.

So, the size of atom is of the order 10^{-10} m

i.e. one angstrom ($1 \text{ \AA} = 10^{-10}$ m).

States of Matter

Solids are the substances which have definite shape, size and volume. In solid, the interatomic spacing is least (about $2 \text{ \AA}$) and interatomic force of attraction is maximum.

Liquids are the substances which have definite volume but no definite shape and size. In liquid, the interatomic spacing is greater in comparison to solid but less in comparison to gas and interatomic force of attraction is relatively weaker in comparison to solid. This enables liquid to flow.

Gases are the substances which do not have fixed shape, size and volume. In gases, the interatomic spacing is maximum (about $10 \text{ \AA}$). Interatomic force of attraction is least in comparison to solids and liquids.

Motion of Molecules in a Gas

The average distance, a molecule can travel without colliding is called the **mean free path** (discussed later in detail). The mean free path in gases is of the order of thousands of Angstrom, due to this reason, atoms of gases are much free to move and can travel long distances without colliding. Due to this property of gases, they get dispersed away if they are not enclosed.

Modern theories had proved that atoms are no longer indivisible or elementary. Every atom consists of nucleus and electrons, the nucleus itself is made up of protons and neutrons, protons and neutrons are again made up of quarks. It may be possible in future that quarks may be further subdivided into some sort of elementary particles.

BEHAVIOUR OF GASES

Nature of gases are easier to understand as the molecules are far from each other and their mutual interactions are negligible except when two molecules collide.

So, gases at low pressure and high temperature much above that at which they liquify (or solidify) follow a relation.

$$pV = KT \quad \dots(i)$$

where, p = pressure and V = volume.

T is absolute temperature (i.e. in Kelvin scale)

K is a constant that varies with volume or with number of atoms or molecules (N) of gas in the given sample.

K can also be written as $K = Nk$...(ii)

The observation tells that k is same for all gases and is denoted by k_B .

So, Eq. (ii) becomes $K = Nk_B$...(iii)

where, k_B = Boltzmann constant and its value in SI unit is 1.38×10^{-23} J/K

From Eqs. (i) and (iii), we have

$$pV = Nk_B T$$

or $\frac{pV}{NT} = k_B = \text{constant}$

So, for different gases, we may write

$$\frac{p_1 V_1}{N_1 T_1} = \frac{p_2 V_2}{N_2 T_2} = \frac{p_3 V_3}{N_3 T_3} \dots = k_B = \text{constant}$$

If p , V and T are same, then N will be same for all gases and this is **Avogadro's hypothesis**.

In other word, according to Avogadro's hypothesis, equal volumes of all gases under identical conditions of pressure and temperature will contain equal number of molecules.

It is established that 22.4 L of any gas at STP (Standard Temperature 273 K and Pressure 1 atm) contain same number of molecules and is represented by N_A .

Avogadro's number (N_A) = 6.023×10^{23} .

The perfect gas equation can be written as,

$$pV = \mu RT$$

where, μ is number of moles and $R = N_A k_B$ is universal constant and T is absolute temperature in kelvin.

$$\mu = \frac{M}{M_0} = \frac{N}{N_A}$$

where, M = mass of the gases

In terms of density, perfect gas equation is

$$p = \frac{\rho RT}{M_0}$$

where, ρ = mass density of the gas,

M_0 = molar mass of the gas,
(mass of one mole of the gas)

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

and k_B = Boltzmann's constant = $1.38 \times 10^{-23} \text{ J/K}$.

Note

- The mass of 22.4 L of any gas at STP is equal to its molecular weight in grams. This amount is called **one mole**.
- 1 mole of a substance contains 6.023×10^{23} atoms or molecules.
- 22.4 L of any gas at STP contains 1 mole of atoms or molecules.

EXAMPLE [1] Applying the Perfect Gas Equation

A vessel contains two non-reacting gases, i.e. neon (monoatomic) and oxygen (diatomic). The ratio of their partial pressures is 3 : 2. Estimate the ratio of (i) number of molecules and (ii) mass density of neon and oxygen in the vessel. Atomic number of Ne = 20.2, molecular mass of O_2 = 32.0. [NCERT]

Sol. (i) As V and T are same for the two gases, we can write

$$\begin{aligned} \text{and } p_{Ne} V &= \mu_{Ne} RT \\ p_{O_2} V &= \mu_{O_2} RT \\ \text{or } \frac{p_{Ne}}{p_{O_2}} &= \frac{\mu_{Ne}}{\mu_{O_2}} \\ \therefore \frac{p_{Ne}}{p_{O_2}} &= \frac{3}{2} \Rightarrow \frac{\mu_{Ne}}{\mu_{O_2}} = \frac{3}{2} \end{aligned}$$

If N_{Ne} and N_{O_2} are the number of molecules of the two gases and N_A is Avogadro's number, then

$$\begin{aligned} \frac{\mu_{Ne}}{\mu_{O_2}} &= \frac{N_{Ne}/N_A}{N_{O_2}/N_A} = \frac{3}{2} \\ \Rightarrow \frac{N_{Ne}}{N_{O_2}} &= 1.5 \end{aligned}$$

$$\begin{aligned} \text{(ii) Now, } \mu_{O_2} &= \frac{m_{O_2}}{M_{O_2}} \text{ and } \mu_{Ne} = \frac{m_{Ne}}{M_{Ne}} \\ \therefore \frac{\rho_{Ne}}{\rho_{O_2}} &= \frac{m_{Ne}/V}{m_{O_2}/V} = \frac{m_{Ne}}{m_{O_2}} = \frac{\mu_{Ne} M_{Ne}}{\mu_{O_2} M_{O_2}} \\ &= \frac{3}{2} \times \frac{20.2}{32} = 0.947 \end{aligned}$$

EXAMPLE [2] Fractional Change in Volume of Water Vapour

The density of water is 1000 kg m^{-3} . The density of water vapour at 100°C and 1 atm pressure is 0.6 kg m^{-3} . The volume of a molecule multiplied by the total number gives, which is called, molecular volume. Estimate the ratio of the molecular volume to the total volume occupied by the water vapour under the above conditions of temperature and pressure. [NCERT]

Sol. For a given mass of water molecule i.e.

$$\text{Volume} \propto \frac{1}{\text{Density}}$$

$\therefore$ Ratio of the molecular volume to the total volume of water vapour

$$\begin{aligned} &= \frac{\text{Density of water vapour}}{\text{Density of water}} \\ &= \frac{0.6 \text{ kg m}^{-3}}{1000 \text{ kg m}^{-3}} = 6 \times 10^{-4} \end{aligned}$$

EXAMPLE [3] Molecular Volume of a Water

Estimate the volume of a water molecule using the data in example 2. [NCERT]

Sol. Molecular mass of water = 18

$\therefore$ Number of molecules in 18 g or 0.018 kg of water
 $= 6 \times 10^{23}$

$$\begin{aligned} \text{Mass of 1 molecule of water} &= \frac{0.018}{6 \times 10^{23}} \\ &= 3 \times 10^{-26} \text{ kg} \end{aligned}$$

In the liquid phase, the molecules of water are closely packed, so density of water molecules may be taken equal to the density of bulk water = 1000 kg m^{-3}

$$\begin{aligned} \therefore \text{Volume of a water molecule} &= \frac{\text{Mass}}{\text{Density}} \\ &= \frac{3 \times 10^{-26}}{1000} \\ &= 3 \times 10^{-29} \text{ m}^3 \end{aligned}$$

EXAMPLE [4] Interatomic Distance in Water Molecule

What is the average distance between atoms in water?

Use the data given in examples 2 and 3. [NCERT]

Sol. Volume of water in vapour state

$$\begin{aligned} &= \frac{1}{6 \times 10^{-4}} \times (\text{volume of water in liquid state}) \\ &= 1.67 \times 10^3 \times \text{volume of water in liquid state} \end{aligned}$$

This is also the increase in amount of volume available for each molecule of water.

When volume V increases by 10^3 times, then radius increases by $V^{1/3}$ or 10 times.

But volume of a water molecule

$$\frac{4}{3} \pi r^3 = 3 \times 10^{-29} \text{ m}^3$$

$$\begin{aligned} \therefore r &= \left(\frac{9}{4\pi} \times 10^{-29} \right)^{1/3} \\ &= 2 \times 10^{-10} \text{ m} = 2 \text{ \AA} \end{aligned}$$

Increased radius = $10 \times 2 = 20 \text{ \AA}$

Average distance = $2 \times \text{Increased radius} = 40 \text{ \AA}$

EXAMPLE [5] Ratio of Number of Molecules

Two non-reactive gases are kept in a container. The ratio of their partial pressures is given 5 : 3. Find the ratio of number of molecules.

Sol. As two non-reactive gases are mixed in a container, so the value of V and T will be same for both with partial pressures, p_1 and p_2 .

$$\text{For gas I } p_1 V = \mu_1 RT \quad \dots(i)$$

$$\text{For gas II } p_2 V = \mu_2 RT \quad \dots(ii)$$

Dividing Eq. (i) by Eq. (ii), we get

$$\frac{p_1}{p_2} = \frac{\mu_1}{\mu_2} \quad \dots(iii)$$

$$\mu_1 = N_1 / N_A \quad \dots(iv)$$

$$\mu_2 = N_2 / N_A \quad \dots(v)$$

Dividing Eq. (iv) by Eq. (v)

$$\frac{\mu_1}{\mu_2} = \frac{N_1}{N_2} \quad \dots(vi)$$

From Eqs. (iii) and (vi), we get

$$\frac{N_1}{N_2} = \frac{\mu_1}{\mu_2} = \frac{p_1}{p_2} \Rightarrow \frac{N_1}{N_2} = \frac{p_1}{p_2} \text{ or } \frac{N_1}{N_2} = \frac{5}{3}$$

Behaviour of Real Gas and Ideal Gas

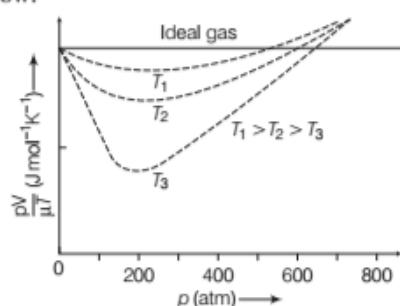
An ideal gas is a theoretical model of a gas and no real gas is truly ideal. However, a real gas behaves as an ideal gas most closely at low pressure and high temperature. This is because at low pressure and high temperature, the molecules of gas are far apart due to which molecular force of attraction is negligible.

As $pV = \mu RT$ (ideal gas equation)

where, μ is the number of moles of the gas and $R = N_A k_B$ = universal constant, called gas constant for one gram mole of the gas.

$$\therefore \frac{pV}{\mu T} = R = \text{constant}$$

There is a graph drawn between $\frac{pV}{\mu T}$ and p as shown in the figure below.



Behaviour of real gases approach ideal gas at low pressure and high temperature

If we plot same graph for real gases at three different temperatures T_1, T_2, T_3 ($T_1 > T_2 > T_3$), then we find the curve as shown in figure by dotted lines.

Solid line showing ideal gas approach and dotted line showing real gas approach. From the observation of this graph, we will find that all curves for real gas approach ideal gas behaviour at low pressure and high temperature.

LAWS FOR AN IDEAL GAS

Boyle's Law

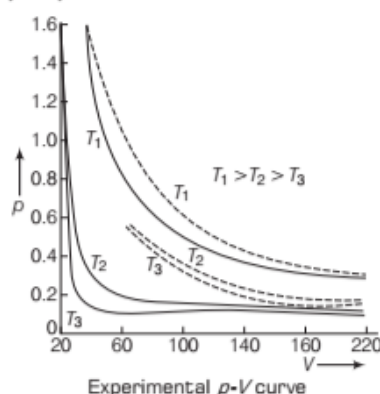
It states that for a given mass of a gas at constant temperature, the volume of that mass of gas is inversely proportional to its pressure, i.e. $V \propto \frac{1}{p}$

According to ideal gas equation, we get $pV = \mu RT$

At constant temperature, $pV = \text{constant}$

$$\Rightarrow \text{Boyle's law, } p_1 V_1 = p_2 V_2 = p_3 V_3 \dots = \text{constant}$$

The figure below shows the comparison between experimental p - V curves and the theoretical curves predicted by Boyle's law.



EXAMPLE [6] Change in Volume

A gas at 27°C in a cylinder has a volume of 4 L and pressure 100 N/m^2 . If the gas is first compressed at constant temperature so that the pressure is 150 N/m^2 . Estimate the change in volume.

Sol. Given, $V_1 = 4 \text{ L}$, $V_2 = ?$, $p_1 = 100 \text{ N/m}^2$
 $p_2 = 150 \text{ N/m}^2$, $\Delta V = ?$

Using Boyle's law for constant temperature, we have

$$\begin{aligned} p_1 V_1 &= p_2 V_2 \\ \Rightarrow V_2 &= \frac{p_1 V_1}{p_2} = \frac{100 \times 4}{150} = 2.667 \text{ L} \end{aligned}$$

$$\therefore \text{Change in volume, } \Delta V = V_1 - V_2 = 4 - 2.667 = 1.33 \text{ L}$$

Charles' Law

It states that for a given mass of an ideal gas at constant pressure, volume (V) of a gas is directly proportional to its absolute temperature T , i.e.

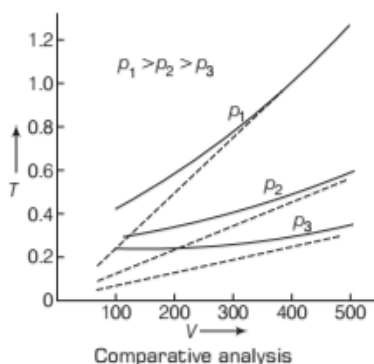
$$V \propto T$$

From ideal gas equation, $\frac{V}{T} = \frac{\mu R}{p}$

At constant pressure, $\frac{V}{T} = \text{constant}$

$$\Rightarrow \text{Charles' law, } \frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \dots = \text{constant}$$

The figure below shows the comparison between experimental T - V curves and the theoretical curves predicted by Charles' law.



EXAMPLE [7] Change in Temperature

A gas is filled in a cylinder at 300K. Calculate the temperature upto which it should be heated so that its volume becomes $\frac{4}{3}$ of its initial volume.

Sol. Given, $T_1 = 300 \text{ K}$, $T_2 = ?$

$$V_1 = V, V_2 = \frac{4}{3}V$$

According to Charles' law, we get

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$

$$\Rightarrow T_2 = T_1 \frac{V_2}{V_1} = 300 \times \frac{4}{3} = 400 \text{ K}$$

Dalton's Law of Partial Pressure

It states that the total pressure of a mixture of non-interacting ideal gases is equal to the sum of partial pressures exerted by individual gases in the mixture.

i.e.
$$p = p_1 + p_2 + p_3 + \dots$$

Consider a mixture of non-interacting ideal gases. Let gas 1 has μ_1 moles, gas 2 has μ_2 moles and so on.

Suppose the net volume of the mixture is V , temperature of mixture is T and pressure of mixture is p .

Equation of state for the mixture

$$pV = (\mu_1 + \mu_2 + \dots) RT$$

$$p = \frac{\mu_1 RT}{V} + \frac{\mu_2 RT}{V} + \dots$$

Dalton's law, $p = p_1 + p_2 + p_3 + \dots$

Here, $p_1 = \frac{\mu_1 RT}{V}$ is the pressure of gas 1 would exert at the same condition of volume and temperature if no other gases are present.

Graham's Law of Diffusion

It states that the rate of diffusion of a gas is inversely proportional to the square root of its density.

$$r \propto \frac{1}{\sqrt{\rho}} \quad \dots(i)$$

where, r = rate of diffusion and ρ = density of the gas.

From the ideal gas equation, $pV = \mu RT$

$$= \frac{M}{M_0} RT$$

$$\Rightarrow \frac{M}{V} = \frac{pM_0}{RT} \quad \dots(ii)$$

where, M = mass of gas

and M_0 = molecular mass of gas

$$\text{Density of gas, } \rho = \frac{M}{V}$$

From Eq. (ii), we get

$$\rho = \frac{pM_0}{RT} \quad \dots(iii)$$

From Eqs. (i) and (iii), we get

$$r \propto \frac{1}{\sqrt{M_0}}$$

Let r_1 and r_2 be the rates of diffusion of gases 1 and 2 respectively, then

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_{02}}{M_{01}}}$$

where, ρ_1 is density of gas 1 and ρ_2 is density of gas 2.

EXAMPLE [8] Identifying the Gas

From a certain apparatus, the diffusion rate of hydrogen has an average value of $28.7 \text{ cm}^3 \text{ s}^{-1}$. The diffusion of another gas under the same conditions is measured to have an average rate of $7.2 \text{ cm}^3 \text{ s}^{-1}$. Identify the gas. [NCERT]

Sol. According to Graham's law of diffusion, we get

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

where, r_1 = rate of diffusion of hydrogen = $28.7 \text{ cm}^3 \text{ s}^{-1}$

r_2 = rate of diffusion of unknown gas = $7.2 \text{ cm}^3 \text{ s}^{-1}$

M_1 = molecular mass of hydrogen = 2 unit

M_2 = molecular mass of unknown gas = ?

$$\therefore \frac{28.7}{7.2} = \sqrt{\frac{M_2}{2}} \Rightarrow M_2 = \left(\frac{28.7}{7.2}\right)^2 \times 2 = 31.78 \approx 32$$

which is molecular mass of oxygen. So, unknown gas is oxygen.

EXAMPLE [9] Pressure Exerted on an Air Bubble

An air bubble of volume 1.0 cm^3 rises from the bottom of a lake 40 m deep at a temperature of 12°C . To what volume does it grow when it reaches the surface, which is at a temperature of 35°C ?

Given, 1 atm = $1.01 \times 10^5 \text{ Pa}$.

[NCERT]

Sol. Initially, when air bubble is at 40 m deep. Then,

$$V_1 = 1 \text{ cm}^3 = 1 \times 10^{-6} \text{ m}^3,$$

$$T_1 = 12^\circ = 273 + 12 = 285 \text{ K}$$

$$p_1 = 1 \text{ atm} + h_1 \rho g$$

$$= 1.01 \times 10^5 + 40 \times 10^3 \times 9.8 = 493000 \text{ Pa}$$

Firstly, when air bubble reaches at the surface, then

$$T_2 = 35^\circ\text{C} = 273 + 35 = 308 \text{ K}$$

$$p_2 = 1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}, V_2 = ?$$

$$\text{As we know, } \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \Rightarrow V_2 = \frac{p_1 V_1 T_2}{T_1 p_2}$$

Final volume i.e.

$$V_2 = \frac{(493000) \times (1 \times 10^{-6}) \times 308}{285 \times 1.01 \times 10^5} \\ = 5.275 \times 10^{-6} \text{ m}^3$$

Work Done on Compressing a Gas

The expansion and compression of ideal gases follow the expression.

$$pV^n = \text{constant} \quad \dots(i)$$

where n is number of moles of the gas. Ideal gases also follow the combined gas law

$$\frac{pV}{T} = \text{constant} \quad \dots(ii)$$

Dividing Eq. (i) by $\frac{pV}{T}$, we get

$$pV^n \div \frac{pV}{T} = \text{constant} \quad \dots(iii)$$

$$\Rightarrow pV^n \cdot \frac{T}{pV} = \text{constant} \quad \dots(iv)$$

$$\Rightarrow TV^{n-1} = \text{constant} \quad \dots(v)$$

Eq. (ii) can now be rewritten as

$$V = \text{constant} \cdot \frac{T}{p} \quad \dots(vi)$$

Putting this value in Eq. (i), we get

$$\frac{pT^n}{p^n} = \text{constant} \quad \dots(vii)$$

$$\Rightarrow \frac{T}{p^{\frac{n-1}{n}}} = \text{constant} \quad \dots(viii)$$

Work done by a gas which is compressing from state 1 to state 2 is given by

$$W = -\int_1^2 p dV \quad \dots(ix)$$

From Eq. (i), we have

$$p = \frac{C}{V^n} \quad \dots(x)$$

Putting this value in equation (ix), we get

$$W = -\int_1^2 V^{-n} dV \quad \dots(xi)$$

On integration it leads to

$$W = C \left(\frac{V^{-n+1}}{-n+1} \right) \Big|_1^2 \quad \dots(xii)$$

Using equation $pV^n = C$, we have

$$W = - \left(pV^n \frac{V^{1-n}}{1-n} \right) \Big|_1^2 \quad \dots(xiii)$$

$$W = - \left(\frac{pV}{1-n} \right) \Big|_1^2 \quad \dots(xiv)$$

$$\Rightarrow W = - \frac{(p_2 V_2 - p_1 V_1)}{1-n} \quad \dots(xv)$$

Ideal gas law also follows the equation

$$p_1 V_1 = mRT_1 \quad \dots(xvi)$$

$$p_2 V_2 = mRT_2 \quad \dots(xvii)$$

Work done now becomes

$$W = - \frac{mR(T_2 - T_1)}{1 - n} \quad \dots(\text{xviii})$$

Note Similar expressions are obtained by similar methods for work done during expansion of gas but starting from

$$W = \int_1^2 p dV$$

We obtain,

$$W = \frac{p_2 V_2 - p_1 V_1}{n - 1}$$

$$W = \frac{mR(T_2 - T_1)}{n - 1}$$

KINETIC THEORY OF IDEAL GAS

The main founders of kinetic theory of gases are

- (i) James Clerk Maxwell (1831-1879), a Scottish physicist
- (ii) Ludwig Boltzmann (1844-1906) from Austria.

Kinetic theory of gases is based on the molecular picture of matter. It correlates the macroscopic properties (e.g. pressure and temperature) of gases to microscopic properties (e.g. speed and kinetic energy) of gas molecules.

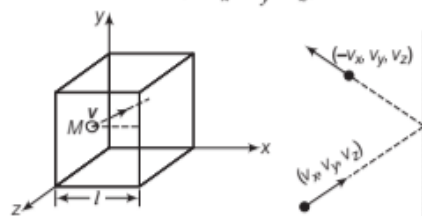
Assumptions of Kinetic Theory of Gases

- (i) A given amount of gas consists of a very large number of molecules (of the order of Avogadro's number 10^{23}) and all molecules are identical in all respect.
- (ii) The molecules of a gas are in a state of incessant random motion in all directions with different speeds, move freely in straight lines following Newton's first law.
- (iii) The size of a molecule is much smaller than the average separation between the molecules. At ordinary pressure and temperature, the average distance between molecules is about $20 \text{ \AA}$, whereas size of a molecule is $2 \text{ \AA}$.
- (iv) There is no intermolecular forces between molecules of gas except during collision.
- (v) The collision between molecules among themselves or between molecules and walls are perfectly elastic (i.e. total momentum and total kinetic energy of molecules are conserved, however only their velocities will change).
- (vi) The duration of collision between two molecules is negligible as compared to time interval of two successive collisions, i.e. collisions are instantaneous.
- (vii) The density and the distribution of molecules is uniform throughout the gas.

Pressure of an Ideal Gas

Consider an ideal gas consisting of N molecules in a container of volume V . The container is a cube with edges of length l . Consider a molecule of mass m moving with velocity (v_x, v_y, v_z) .

As molecule collides with the wall parallel to yz -plane elastically, its x -component of velocity is reversed, while its y and z -components of velocity remain unaltered i.e. velocity after collision is $(-v_x, v_y, v_z)$.



Elastic collision of a gas molecule along x -component of velocity

So, the change in momentum of the molecule is

$$\Delta p_x = (p_x)_{\text{final}} - (p_x)_{\text{initial}}$$

$$\Delta p_x = -mv_x - (mv_x)$$

$$\Delta p_x = -2mv_x$$

$\therefore$ Impulse = Change in momentum of molecule

$$\Rightarrow F \Delta t = \Delta p_x = -2mv_x \quad \dots(i)$$

where, F is the average force on the molecule by the wall.

For molecule to collide with same wall, twice it must travel a distance $2l$ in x -direction (as the molecule has to travel from $+x$ to $-x$ -directions between two walls).

So, time interval between two collisions with same wall is

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

The average force exerted on a molecule by the wall for each collision is

$$F = \frac{-2mv_x}{\Delta t} = \frac{(-2mv_x)}{(2l/v_x)} = \frac{-mv_x^2}{l}$$

By Newton's Third Law,

The average force exerted by a molecule on the wall is $\frac{mv_x^2}{l}$. If there are N molecules, so total force on the wall

$$\text{will be } F_{\text{wall}} = \frac{m}{l} (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2)$$

It can be rewritten as

$$F_{\text{wall}} = \frac{Nm}{l} \bar{v}_x^2 \quad \dots(ii)$$

where,
$$\bar{v}_x^2 = \frac{v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2}{N}$$

Now,
$$\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$$

[as velocity has 3 components v_x, v_y, v_z]

Since, motion is completely random, so average values $\bar{v}_x^2, \bar{v}_y^2$ and $\bar{v}_z^2$ are equal to each other [i.e. $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2$]

$$\therefore \bar{v}^2 = 3\bar{v}_x^2 \text{ or } \bar{v}_x^2 = \frac{1}{3}\bar{v}^2 \quad \dots(\text{iii})$$

From Eqs. (ii) and (iii), we get,
$$F_{\text{wall}} = \frac{N}{3} \left(\frac{m}{l} \bar{v}^2 \right) \quad \dots(\text{iv})$$

Here, F_{wall} is normal force on the wall.

Pressure on the wall,
$$p = \frac{F_{\text{wall}}}{\text{Area}} = \frac{F_{\text{wall}}}{l^2}$$

$$\Rightarrow p = \frac{1}{l^2} \left(\frac{N}{3} \frac{m \bar{v}^2}{l} \right) \text{ or } p = \frac{1}{l^3} \left(\frac{Nm \bar{v}^2}{3} \right)$$

or,
$$p = \frac{1}{V} \left(\frac{Nm \bar{v}^2}{3} \right) \quad [\because \text{volume } V = l^3]$$

or,
$$p = \frac{1}{3} \left(\frac{N}{V} \right) m \bar{v}^2$$

$$\Rightarrow \text{Pressure exerted by an ideal gas, } p = \frac{1}{3} nm \bar{v}^2 \quad \dots(\text{v})$$

where, p = pressure exerted on wall,

n = number density (i.e. number of molecules per unit volume) of gas,

m = mass of one molecule,

$\bar{v}^2$ = mean square speed

v = mean square speed

and $p = \frac{1}{3} nm \bar{v}^2$ is known as expression for pressure exerted by an ideal gas and also called **kinetic gas equation**.

From the above derivations, we conclude

- The shape of vessel is immaterial because area A and time interval Δt do not appear in the final result. For a vessel of arbitrary shape, we can always choose a small infinitesimal planar area and carry through all the steps.
- As per Pascal's law, pressure in one portion of the container as the gas in equilibrium is the same as anywhere else.
- In this derivation, we have ignored any collisions amongst molecules. It can be shown that if these collisions are not too frequent and the time spent in such collision is negligible compared to time between collisions, then mutual molecular collisions do not affect the final result.

Relation between Pressure exerted by an Ideal Gas and its Density

Let M be the mass of all molecules of a given ideal gas enclosed in a vessel of volume V having density ρ , then

$$\begin{aligned} n \times m &= \text{Number of molecules per unit volume} \\ &\times \text{mass of one molecule} \\ &= \text{Total mass of all molecules per unit volume} \\ &= \frac{M}{V} \end{aligned}$$

$$\Rightarrow n \times m = \rho \quad \left[\because \text{Density } [\rho] = \frac{\text{Mass}}{\text{Volume}} \right] \dots(\text{vi})$$

From Eqs. (v) and (vi), we get

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

EXAMPLE |10| Behaviour of an Ideal Gas

A container is filled with a gas at a pressure of 76 cm of mercury at a certain temperature. The mass of a gas is increased by 50% by introducing more gas in the container at same temperature. Calculate the final pressure of the gas.

Sol. According to kinetic theory of gases,

$$pV = \frac{1}{3} M v_{\text{rms}}^2$$

At constant temperature, v_{rms}^2 is constant. As V is also constant.

$$\therefore p \propto M$$

When the mass of the gas is increased by 50%, pressure also increased by 50%.

$$\therefore \text{Resultant pressure} = 76 + \frac{50}{100} \times 76 = 114 \text{ cm of Hg}$$

Kinetic Interpretation of Temperature

The average KE of a molecule depends on the absolute temperature of the gas. It is the kinetic interpretation of temperature. Let us consider a sample of an ideal gas having N number of molecules. Let the volume of the gas is V , pressure is p and temperature is T .

From the pressure expression of an ideal gas

$$p = \frac{1}{3} nm \bar{v}^2 \quad \dots(\text{i})$$

Multiplying both sides with V , we get

$$\Rightarrow pV = \frac{1}{3} (nV) m \bar{v}^2$$

or,
$$pV = \frac{2}{3} (nV) \frac{1}{2} m \bar{v}^2$$

$$\Rightarrow pV = \frac{2}{3} N \left(\frac{1}{2} m \bar{v}^2 \right) \quad \dots(\text{ii})$$

Here, number of molecules in the sample, $N = nV$

Here, $\frac{1}{2}m\bar{v}^2$ is the average kinetic energy of the molecules of the gas.

So, total internal energy of the gas

$$E = N \left(\frac{1}{2} m \bar{v}^2 \right) \quad \dots(\text{iii})$$

From Eqs. (ii) and (iii), we get

$$pV = \frac{2}{3} E \quad \dots(\text{iv})$$

For ideal gas, we can write

$$pV = \mu RT$$

$$\text{or, } pV = \mu k_B N_A T = k_B (\mu N_A) T$$

$$\text{or, } pV = k_B NT \quad \dots(\text{v})$$

$$[N = \mu N_A = \text{total number of molecules}]$$

Combining Eqs. (iv) and (v), we get

$$\frac{2}{3} E = k_B NT \Rightarrow \frac{E}{N} = \frac{3}{2} k_B T \quad \dots(\text{vi})$$

$$\text{or } \frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T \quad \dots(\text{vii})$$

$$\Rightarrow \text{Average kinetic energy, } \frac{1}{2} m \bar{v}^2 \propto T$$

It is clear that average kinetic energy of a molecule is directly proportional to the absolute temperature of the gas. It is independent of pressure, volume and the nature of the ideal gas. This is a fundamental result that relates temperature of the gas to average kinetic energy of a molecule.

If $T = 0$, then $\frac{1}{2} m \bar{v}^2 = 0$ but $m \neq 0$ so $\bar{v}^2 = 0$

Thus, absolute zero of temperature may be defined as that temperature at which the mean square speed of the gas molecules reduces to zero.

Root Mean Square Speed

The square root of the mean square speed $\bar{v}^2$ is known as root mean square speed.

From kinetic interpretation,

$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T$$

$$\text{So, } \bar{v}^2 = \frac{3 k_B T}{m}$$

Taking square root of both the sides

$$\sqrt{\bar{v}^2} = \sqrt{\frac{3 k_B T}{m}}$$

$$\text{Root mean square speed, } v_{\text{rms}} = \sqrt{\frac{3 k_B T}{m}}$$

where, m = mass of one molecule,

k_B = Boltzmann constant

and T = absolute temperature.

EXAMPLE [11] Energy Stored in a Balloon

A balloon has 5.0 g mole of helium at 7°C. Calculate

(i) the number of atoms of helium in the balloon.

(ii) the total internal energy of the system.

[NCERT Exemplar]

Sol. (i) Here, $\mu = 5.0$, $T = 7^\circ\text{C} = 273 + 7 = 280\text{ K}$

$$\begin{aligned} \text{Number of atoms} &= \mu N_A = 5.0 \times 6.02 \times 10^{23} \\ &= 30 \times 10^{23} \end{aligned}$$

(ii) Average kinetic energy per molecule = $\frac{3}{2} k_B T$

$$\therefore \text{Total internal energy} = \frac{3}{2} k_B T \times N$$

$$= \frac{3}{2} \times 30 \times 10^{23} \times 1.38 \times 10^{-23} \times 280 = 1.74 \times 10^4 \text{ J}$$

EXAMPLE [12] Root Mean Square Speed

In a container, two gases neon and argon are filled. Find the ratio of the root mean square speed of the molecules of the two gases. $M_{\text{Ne}} = 20.2$ and $M_{\text{Ar}} = 39.9$. The temperature of the system is 30°C.

Sol. Given, $M_{\text{Ne}} = 20.2$, $M_{\text{Ar}} = 39.9$

Temperature (T) = 30°C

$$\text{We know that, } \frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} k_B T$$

Temperature is same for both the gases. Now, we can find the ratio of v_{rms} for the two gases.

$$\frac{(v_{\text{rms}})_{\text{Ne}}}{(v_{\text{rms}})_{\text{Ar}}} = \frac{(M)_{\text{Ar}}}{(M)_{\text{Ne}}}$$

Now, we can easily find the numerical value of ratio of two v_{rms} .

$$\frac{(v_{\text{rms}})_{\text{Ne}}}{(v_{\text{rms}})_{\text{Ar}}} = \sqrt{\frac{39.9}{20.2}} \approx 1.40$$

Maxwell's Speed Distribution

In a given sample of gas, all molecules don't move with same speed. They move randomly in different directions, but the distribution of velocities among the molecules remain fixed. Maxwell first studied molecular speed distribution and derived an equation giving distribution of molecules as follows.

If dN represents the number of molecules having speed between v and $v + dv$ then,

$$dN = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}} dv$$

where, v = molecular speed of the gas,

m = the molecular mass of the gas,

T = temperature of the gas in kelvin,

N = total number of molecules of the gas

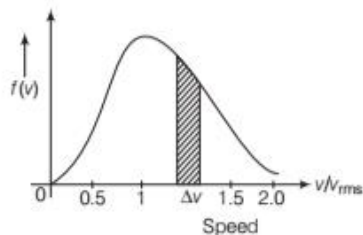
and k_B = Boltzmann constant.

The fraction of molecules with speed v and dv is equal to area of strip shown in figure,

$$\text{i.e. } \frac{dN}{N} = f(v) dv = \text{area of the strip}$$

Total area of the curve will be unity, as it represents all molecules.

Above figure shows the Maxwell's distribution function $f(v)$ of a gas at three different temperatures. Each



graph has a peak which represents the maximum fraction of total molecules having maximum speed ($v_{\max}$) due to this reason $v_{\max}$ is also called most probable speed. As the temperature increases, the curve become flatter and its maximum points (peak points) shifts towards higher speed.

Note

- **Most probable speed** The speed possessed by the maximum number of molecules in a gas at a given temperature.

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

- **Mean or Average speed** The arithmetic mean of the speed of the molecules of a gas at a given temperature.

$$v_{av} = \sqrt{\frac{8k_B T}{\pi m}}$$

EXAMPLE [13] RMS Speed of a Gas Molecule

The molecules of a given mass of a gas have root mean square speeds of 100 ms^{-1} at 27°C and 1.00 atm pressure. What will be the root mean square speeds of the molecules of

the gas at 127°C and 2.0 atm pressure? [NCERT Exemplar]

Sol. According to ideal gas equation, we get

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

$$\text{or } \frac{V_1}{V_2} = \frac{p_2 T_1}{p_1 T_2} = \frac{2 \times 300}{1 \times 400} = \frac{3}{2}$$

$$p_1 = \frac{1}{3} \frac{M}{V_1} (v_{rms})_1^2, \quad p_2 = \frac{1}{3} \frac{M}{V_2} (v_{rms})_2^2$$

$$\therefore (v_{rms})_2^2 = (v_{rms})_1^2 \times \frac{V_2}{V_1} \times \frac{p_2}{p_1} = (100)^2 \times \frac{2}{3} \times 2$$

$$\text{or } (v_{rms})_2 = \frac{200}{\sqrt{3}} \text{ m s}^{-1}$$

EXAMPLE [14] A Nuclear Fission

Uranium has two isotopes of masses 235 and 238 units. If both are present in uranium hexafluoride gas, which would have the larger average speed? If atomic mass of fluorine is 19 units, estimate the percentage difference in speeds at any temperature. How is the above concept of difference in speeds utilised in the enrichment of uranium needed for nuclear fission? [NCERT]



At a fixed temperature, the average energy $= \frac{1}{2} m v_{rms}^2$ is

constant. So, smaller the mass of a molecule, faster will be its speed. Clearly,

$$\text{Speed of molecule} \propto \frac{1}{\sqrt{\text{molecular mass}}}$$

Sol. Molecular mass of ^{235}U hexafluoride
 $= 235 + 6 \times 19 = 349$

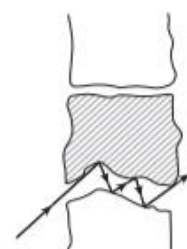
Molecular mass of ^{238}U hexafluoride
 $= 238 + 6 \times 19 = 352$

$$\therefore \frac{v_{349}}{v_{352}} = \left(\frac{352}{349} \right)^{1/2} = 1.0044$$

Percentage difference in speeds,

$$\frac{\Delta v}{v} \times 100 = 0.0044 \times 100 = 0.44\%$$

^{235}U is the isotope needed for nuclear fission. To separate it from the more abundant isotope ^{238}U , the mixture is surrounded by a porous cylinder. The porous cylinder must be thick and narrow, so that the molecule wanders through individually, colliding with the walls of the long porous, as shown in figure.



A molecule going through a porous wall

The faster molecule will leak out more than the slower one and so there is more of the lighter molecule (enrichment) outside the porous cylinder. The method is not very efficient and has to be repeated several times for sufficient enrichment.

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. Interatomic forces are

- attractive in long range
- repulsive in short range
- negligible in gases
- All (a), (b) and (c)

Sol. (d) Interatomic forces are attractive in long range and repulsive in short range and negligible in gases.

2. According to atomic hypothesis

- (a) atoms attract each other when they are little distance apart
- (b) atoms repel if they being squeezed into one another
- (c) Both (a) and (b)
- (d) Neither (a) nor (b)

Sol. (c) Atoms attract when they are little distance apart and repel, if they being squeezed into one another.

3. Boyle's law is applicable for an [NCERT Exemplar]

- (a) adiabatic process
- (b) isothermal process
- (c) isobaric process
- (d) isochoric process

Sol. (b) Boyle's law is applicable when temperature is constant

$$\text{i.e., } pV = nRT = \text{constant}$$

$$\Rightarrow pV = \text{constant (at constant temperature)}$$

$$\text{i.e., } p \propto \frac{1}{V} \quad [\text{where } p = \text{pressure, } V = \text{volume}]$$

So, this process can be called as isothermal process.

4. The collisions of the molecules of an ideal gas are

- (a) elastic
- (b) inelastic
- (c) completely inelastic
- (d) partially elastic

Sol. (a) According to kinetic theory of gases the collision among molecules and the collision of molecule with the walls of container are elastic.

5. The root mean square speed of a nitrogen molecule at 300K is

- (a) $\sqrt{534} \text{ ms}^{-1}$
- (b) 534 ms^{-1}
- (c) 267 ms^{-1}
- (d) $\sqrt{216} \text{ ms}^{-1}$

Sol. (c)
$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 300}{28}}$$

$$= 267.2 \text{ ms}^{-1}$$

VERY SHORT ANSWER Type Questions

6. Under what conditions, real gases behave as an ideal gas?

Sol. At low pressure and high temperature, real gases behave as an ideal gas.

7. Calculate the number of atoms in 39.4 g gold. Molar mass of gold is 197 g mol^{-1} .

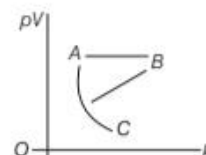
[NCERT Exemplar]

Sol. Molar mass of gold is 197 g mol^{-1} , the number of atoms
 $= 6.0 \times 10^{23}$

$\therefore$ Number of atoms in 39.4 g

$$= \frac{6.0 \times 10^{23} \times 39.4}{197} = 1.2 \times 10^{23}$$

8. The given graph shows the variation of p - V versus p graph for different gases at constant temperature.



Which of the following gas is ideal and why?

Sol. Gas A is ideal because pV is constant for gas A so, gas A obeys Boyle's law for all values of pressure.

9. When air is pumped into a cycle tyre, the volume and pressure of the air in the tyre, both are increased. What about Boyle's law in this case? [NCERT Exemplar]

Sol. When air is pumped, more molecules are pumped in Boyle's law, is stated for situation where number of molecules remain constant.

10. The volume of a given mass of a gas at 27°C , 1 atm is 100 cc. What will be its volume at 327°C ? [NCERT Exemplar]

Sol. Keeping p constant, we have

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{100 \times 600}{300} = 200 \text{ cc}$$

11. What is the minimum possible temperature on the basis of Charles' law?

Sol. The minimum possible temperature on the basis of Charles' law is -273.15°C .

12. If a vehicle runs on the road for a long time, then the air pressure in the tyres increases. Explain.

Sol. Due to the presence of friction between the road and tyres, the tyres get heated as a result of which temperature of air inside the tyre increases and hence pressure in tyre also increases.

13. According to kinetic theory of gases, explain absolute zero.

Sol. Absolute zero is the temperature at which the molecules of a gas becomes motionless. i.e. $\bar{v}_{\text{rms}} = 0$

14. Two molecules of a gas have speeds of $9 \times 10^6 \text{ ms}^{-1}$ and $1 \times 10^6 \text{ ms}^{-1}$, respectively. What is the root mean square speed of these molecules? [NCERT Exemplar]

Sol.
$$v_{\text{rms}} = \sqrt{\frac{v_1^2 + v_2^2}{2}} = \sqrt{\frac{(9 \times 10^6)^2 + (1 \times 10^6)^2}{2}}$$

$$= \sqrt{\frac{(81 + 1) \times 10^{12}}{2}} = \sqrt{41} \times 10^6 \text{ ms}^{-1}$$

15. What would be the effect on rms velocity of gas molecules, if the temperature of the gas is increased by a factor 4?

Sol. As, $v_{\text{rms}} \propto \sqrt{T}$

If temperature of the gas is increased 4 times, then v_{rms} will be doubled.

16. If a gas is heated, its temperature increases.
On the basis of kinetic theory of gases, explain.

Sol. If a gas is heated, then the root mean square velocity of its molecules is increased.

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

$\therefore$ The temperature of the gas increases.

SHORT ANSWER Type Questions

17. Molar volume is the volume occupied by 1 mol of any (ideal) gas at standard temperature and pressure (STP: 1 atm pressure, 0°C). Show that, it is 22.4 L. [NCERT]

Sol. As, for one mole of ideal gas, $pV = \mu RT$ [$\mu = 1$]

$$\begin{aligned} pV &= RT \\ \Rightarrow V &= \frac{RT}{p} \end{aligned}$$

Putting, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$, $T = 273 \text{ K}$

$$p = 1 \text{ atm} = 1.013 \times 10^5 \text{ N m}^{-2}$$

$$V = \frac{8.31 \times 273}{1.013 \times 10^5} = 0.0224 \text{ m}^3$$

$$= 22.4 \text{ L} \quad [\because 1 \text{ m}^3 = 10^3 \text{ L}]$$

18. Estimate the total number of air molecules (inclusive of oxygen, nitrogen, water vapour and other constituents) in a room of capacity 25.0 m³ at a temperature of 27°C and 1 atm pressure. ($k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$) [NCERT]

Sol. Given, $V = 25.0 \text{ m}^3$, $T = 273 + 27 = 300 \text{ K}$

$$k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

Now, $pV = \mu RT$

$$\Rightarrow pV = \mu(N_A k_B)T$$

$$\Rightarrow pV = N' k_B T$$

[N' is total number of molecules]

$$\begin{aligned} \therefore N' &= \frac{pV}{k_B T} = \frac{(1.01 \times 10^5) \times 25}{(1.38 \times 10^{-23}) \times 300} \\ &= 6.10 \times 10^{26} \end{aligned}$$

19. Estimate the fraction of molecular volume to the actual volume occupied by oxygen gas at STP. Take the diameter of an oxygen molecule to be 3 Å. [NCERT]

Sol. Given, $d = 3 \text{ Å}$

$$r = \frac{d}{2} = 1.5 \times 10^{-10} \text{ m} = 1.5 \times 10^{-8} \text{ cm}$$

$$\text{Molecular volume, } V = \frac{4}{3} \pi r^3 N$$

$$= \frac{4}{3} \times 3.14 \times (1.5 \times 10^{-8})^3 \times 6.023 \times 10^{23} = 8.52 \text{ cc}$$

Actual volume occupied by 1 mole of oxygen at STP,

$$V' = 22400 \text{ cc}$$

$$\therefore \frac{V}{V'} = \frac{8.52}{22400} = 3.8 \times 10^{-4}$$

20. A flask contains argon and chlorine in the ratio of 2 : 1 by mass. The temperature of the mixture is 27°C. Obtain the ratio of
(i) average kinetic energy per molecule and
(ii) root mean square speed (v_{rms}) of the molecules of the two gases. Atomic mass of argon = 39.9 u; Molecular mass of chlorine = 70.9 u. [NCERT]

Sol. (i) The average kinetic energy per molecule of any gas is $\frac{3}{2} k_B T$. It depends only on temperature and not on the nature of the gas. As both argon and chlorine have the same temperature in the flask, the ratio of average KE per molecule of the two gases is 1 : 1.
(ii) If m is mass of single molecule and M is the molecular mass, then

$$\frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} k_B T$$

= constant at a given temperature

$$\therefore \frac{(v_{\text{rms}}^2)_{\text{Ar}}}{(v_{\text{rms}}^2)_{\text{Cl}_2}} = \frac{(m)_{\text{Cl}_2}}{(m)_{\text{Ar}}} = \frac{M_{\text{Cl}_2}}{M_{\text{Ar}}} = \frac{70.9}{39.9} = 1.777$$

$$\text{or } \frac{(v_{\text{rms}})_{\text{Ar}}}{(v_{\text{rms}})_{\text{Cl}_2}} = \sqrt{1.777} = 1.333$$

21. We have 0.5 g of hydrogen gas in a cubic chamber of size 3 cm kept at NTP. The gas in the chamber is compressed keeping the temperature constant till a final pressure of 100 atm. Is one justified in assuming the ideal gas law, in the final state? (Hydrogen molecules can be considered as spheres of radius 1 Å). [NCERT Exemplar]

Sol. We have, $0.25 \times 6 \times 10^{23}$ molecules, each of volume 10^{-30} m^3 .

$$\text{Molecular volume} = 2.5 \times 10^{-7} \text{ m}^3$$

Supposing, ideal gas law is valid.

$$\text{Final volume} = \frac{V_{\text{in}}}{100} = \frac{(3)^3 \times 10^{-6}}{100} = 2.7 \times 10^{-7} \text{ m}^3$$

Which is about the molecular volume. Hence, intermolecular forces cannot be neglected. Therefore, the ideal gas situation does not hold.

22. Three vessels of equal capacity have gases at the same temperature and pressure. The first vessel contains neon (monoatomic), the second contains chlorine (diatomic) and the third contains uranium hexafluoride (polyatomic). Do the vessels contain equal number of respective molecules?

Is the root mean square speed of molecules, the same in the three cases? If not, in which case is v_{rms} , the largest? [NCERT]

Sol. As three vessels are identical i.e. they have same volume. Now at constant pressure, temperature and volume, the three vessels will contain equal number of molecules (by Avogadro's law) and is equal to Avogadro's number, $N_A = 6.023 \times 10^{23}$.

$$\therefore v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} \Rightarrow v_{\text{rms}} \propto \frac{1}{\sqrt{m}}$$

where, m is mass of single gas molecule as neon has the smallest mass, so rms speed will be greatest in case of neon.

23. A tank used for filling helium balloons has a volume of 0.6 m^3 and contains 2.0 mol of helium gas at 20.0°C . Assuming that the helium behaves like an ideal gas.

- What is the total translational kinetic energy of the molecules of the gas?
- What is the average kinetic energy per molecule?

Sol. (i) We know that $(\text{KE})_{\text{trans}} = \frac{3}{2} nRT$

$$\text{Given, } n = 2 \text{ mol, } T = 273 + 20 = 293 \text{ K} \\ \Rightarrow (\text{KE})_{\text{trans}} = \frac{3}{2} (2) (8.31) (293) = 7.3 \times 10^3 \text{ J}$$

(ii) Average KE per molecule

$$= \frac{1}{2} m \bar{v}_{\text{rms}}^2 = \frac{3}{2} kT = \frac{3}{2} (1.38 \times 10^{-23}) (293) \\ = 6.07 \times 10^{-21} \text{ J}$$

24. At what temperature, is the root mean square speed of an atom in an argon gas cylinder equal to the rms speed of a helium gas atom at -20°C ? (Atomic mass of Ar = 39.9 u , He = 4.0 u). [NCERT]

Sol. Let C and C' be the rms velocity of argon and a helium gas atoms at temperatures TK and $T'K$, respectively.

$$\text{Here, } M = 39.9, M' = 4.0, T = ?, \\ T' = -20 + 273 = 253 \text{ K}$$

$$\text{Now, } v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3RT}{39.9}}$$

$$\text{and } v' = \sqrt{\frac{3RT'}{M'}} = \sqrt{\frac{3R \times 253}{4}}$$

$$\text{Since, } v = v', \text{ therefore } \sqrt{\frac{3RT}{39.9}} = \sqrt{\frac{3R \times 253}{4}}$$

$$\text{or } T = \frac{39.9 \times 253}{4} = 2523.7 \text{ K}$$

25. A gas mixture consists of molecules of types A , B and C with masses, $m_A > m_B > m_C$. Rank the three types of molecules in decreasing order of (i) average KE (ii) rms speed. [NCERT Exemplar]

Sol. The average KE will be same as conditions of temperature and pressure are same.

$$v_{\text{rms}} \propto \frac{1}{\sqrt{m}}$$

$$\therefore m_A > m_B > m_C \\ \Rightarrow v_C > v_B > v_A$$

26. A gas is contained in a closed vessel. How pressure due to the gas will be affected if force of attraction between the molecules disappear suddenly?

Sol. As force of attraction between molecules disappears, then molecules will hit the wall with more speeds, hence, rate of change of momentum will increase.

$$\text{As we know } F = \frac{\Delta p}{\Delta t},$$

where F is average force on the wall due to molecules. Δp is change in momentum and Δt is the time duration. Due to increase in Δp , force F will also increase, hence pressure, $p = \frac{F}{A}$ will increase. Here, A is area of one wall.

LONG ANSWER Type I Questions

27. Write the difference between ideal gas and real gas.

Sol.

Ideal Gas	Real Gas
(i) It obeys ideal gas equation, $pV = \mu RT$ at all temperatures and pressures.	It does not obey, $pV = \mu RT$ at all values of temperature and pressure.
(ii) The volume of the molecules of an ideal gas is zero.	The volume of the molecules of a real gas is non-zero.
(iii) There is no intermolecular force between the molecules.	There is intermolecular force of attraction or repulsion depending on whether intermolecular separation is larger or small.
(iv) There is no intermolecular potential energy (U) because intermolecular force (F) is zero.	Potential energy (U) does not equal to zero as intermolecular force (F) is not zero.
(v) It has only kinetic energy.	It has both kinetic and potential energy.
(vi) At absolute zero, the volume, pressure and internal energy become zero.	All real gases get liquified before reaching absolute zero. The internal energy of the liquified gas is not zero.

28. Estimate the average thermal energy of a helium atom at (i) room temperature (27°C) (ii) the temperature on the surface of the sun (6000 K), (iii) the temperature of 10 million kelvin (the typical core temperature in the case of a star). [NCERT]

 Thermal energy represents that part of internal energy which is translational kinetic in nature. This is equal to $\frac{3}{2}k_B T$; which only depends on absolute temperature of the gas.

Sol. (i) Given, $T = 27^\circ\text{C} = (273.15 + 27) = 300.15\text{ K}$

$$\text{Average thermal energy, } E = \frac{3}{2}k_B T$$

$$(\text{where, } k_B = \text{Boltzmann constant} = 1.38 \times 10^{-23} \text{ J K}^{-1})$$

$$E = \frac{3}{2} \times 1.38 \times 10^{-23} \times 300.15 = 6.21 \times 10^{-21} \text{ J}$$

(ii) At the temperature, $T = 6000\text{ K}$ (surface of the sun)

$$\text{Average thermal energy, } E = \frac{3}{2}k_B T$$

$$= \frac{3}{2} \times 1.38 \times 10^{-23} \times 6000 = 1.241 \times 10^{-19} \text{ J}$$

(iii) At temperature, $T = 10^7\text{ K}$

Average thermal energy,

$$E = \frac{3}{2}k_B T = \frac{3}{2} \times 1.38 \times 10^{-23} \times 10^7 = 2.07 \times 10^{-16} \text{ J}$$

29. (i) Write ideal gas equation in terms of density.
(ii) If molar volume is the volume occupied by 1 mole of any (ideal) gas at STP, show that it is 22.4 L (take $R = 8.313 \text{ mol}^{-1}\text{K}^{-1}$).

Sol. (i) Refer to text on page no. 511.

$$(ii) p = 1 \text{ atm} = 0.76 \text{ m of Hg} = 0.76 \times (13.6 \times 10^3) \times 9.8 \text{ Pa}$$

$$\Rightarrow T = 273 \text{ K, } R = 8.31 \text{ J mol}^{-1}\text{K}^{-1}, \mu = 1 \text{ mole}$$

$$\text{As } pV = \mu RT$$

$$\text{or, } V = \frac{\mu RT}{p} = \frac{1 \times 8.31 \times 273}{0.76 \times (13.6 \times 10^3) \times 9.8} = 22.4 \times 10^{-3} \text{ m}^3 = 22.4 \text{ L}$$

30. Explain, why

- (i) there is no atmosphere on moon.
(ii) there is fall in temperature with altitude.

[NCERT Exemplar]

Sol. (i) The moon has small gravitational force and hence the escape velocity is small. As the moon is in the proximity of the earth as seen from the sun, the moon has the same amount of heat per unit area as that of the earth. The air molecules have large range of speeds.

Even though the rms speed of the air molecules is smaller than escape velocity on the moon, a significant number of molecules have speed greater than escape velocity and they escape.

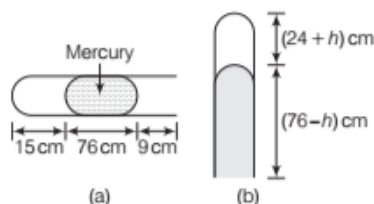
Now, rest of the molecules arrange the speed distribution for the equilibrium temperature. Again, a significant number of molecules escape as their speeds exceed escape speed. Hence, over a long time the moon has lost most of its atmosphere.

- (ii) As the molecules move higher, their potential energy increases and hence kinetic energy decreases and hence temperature reduces.

At greater height, more volume is available and gas expands and hence some cooling takes place.

31. A meter long narrow bore held horizontally (and closed at one end) contains a 76 cm long mercury thread which traps a 15 cm column of air. What happens, if the tube is held vertically with the open end at the bottom? [NCERT]

Sol. If the tube is held horizontally, the mercury thread of length 76 cm traps a length of air = 15 cm. A length of 9 cm of the tube will be at the open end, Fig. (a). The pressure of air enclosed in tube will be atmospheric pressure. Let area of cross-section of the tube be 1 sq. cm.



$$\therefore p_1 = 76 \text{ cm and } V_1 = 15 \text{ cm}^3$$

If the tube is held vertically, 15 cm air gets another 9 cm

of air (filled in the right hand side in the horizontal position) and let h cm of mercury flow out to balance the atmospheric pressure, Fig. (b). Then, the heights of air column and mercury column are $(24 + h)$ cm and $(76 - h)$ cm, respectively.

The pressure of air = $76 - (76 - h) = h$ cm of mercury

$$\therefore V_2 = (24 + h) \text{ cm}^3$$

$$\text{and } p_2 = h \text{ cm}$$

If we assume that temperature remains constant, then

$$p_1 V_1 = p_2 V_2 \text{ or } 76 \times 15 = h \times (24 + h)$$

$$\text{or } h^2 + 24h - 1140 = 0$$

$$\text{or } h = \frac{-24 \pm \sqrt{(24)^2 + 4 \times 1140}}{2}$$

$$= 23.8 \text{ cm or } -47.8 \text{ cm}$$

Since, h cannot be negative (because more mercury cannot flow into the tube), therefore $h = 23.8$ cm. Thus, in the vertical position of the tube, 23.8 cm of mercury flows out.

32. The container shown in figure has two chambers, separated by a partition of volumes $V_1 = 2.0$ L and $V_2 = 3.0$ L. The chambers contain $\mu_1 = 4.0$ and $\mu_2 = 5.0$ moles of a gas at pressures $p_1 = 1.00$ atm and $p_2 = 2.00$ atm. Calculate the pressure after the partition is removed and the mixture attains equilibrium. [NCERT Exemplar]

V_1	V_2
μ_1	μ_2
p_1	p_2

Sol. Given, $V_1 = 2.0$ L, $V_2 = 3.0$ L, $\mu_1 = 4.0$ moles, $\mu_2 = 5.0$ moles

$$p_1 = 1.00 \text{ atm}, p_2 = 2.00 \text{ atm}$$

$$p_1 V_1 = \mu_1 R T_1, p_2 V_2 = \mu_2 R T_2$$

$$\mu = \mu_1 + \mu_2, V = V_1 + V_2$$

$$\text{For 1 mole, } pV = \frac{2}{3} E$$

$$\text{For } \mu_1 \text{ mole, } p_1 V_1 = \frac{2}{3} \mu_1 E_1$$

$$\text{For } \mu_2 \text{ mole, } p_2 V_2 = \frac{2}{3} \mu_2 E_2$$

$$\text{Total energy is } (\mu_1 E_1 + \mu_2 E_2) = \frac{3}{2} (p_1 V_1 + p_2 V_2)$$

$$pV = \frac{2}{3} E_{\text{total}} = \frac{2}{3} \mu E_{\text{per mole}}$$

$$p(V_1 + V_2) = \frac{2}{3} \times \frac{3}{2} (p_1 V_1 + p_2 V_2)$$

$$p = \frac{p_1 V_1 + p_2 V_2}{V_1 + V_2} \quad \dots(i)$$

$$= \left(\frac{1.00 \times 2.0 + 2.00 \times 3.0}{2.0 + 3.0} \right) = \frac{8.0}{5.0} = 1.60 \text{ atm}$$

33. An oxygen cylinder of volume 30 L, has an initial gauge pressure of 15 atm and a temperature of 27 °C. After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atm and its temperature drops to 17 °C. Estimate the mass of oxygen taken out of the cylinder ($R = 8.31 \text{ mol}^{-1} \text{K}^{-1}$, molecular mass of $O_2 = 32$ u). [NCERT]



Whenever masses are taken out of the closed system, no more it is a closed system, hence ideal gas equation should be applied to calculate the change in mass. First, number of moles removed should be calculated and then by multiplying with molecular mass of the gas, the same can be converted into mass of the gas removed.

Sol. Given, absolute pressure, $p_1 = (15 + 1) \text{ atm}$
 $[\because \text{absolute pressure} = \text{gauge pressure} + 1 \text{ atm}]$
 $= 16 \times 1.013 \times 10^5 \text{ Pa}$
 $V_1 = 30 \text{ L} = 30 \times 10^{-3} \text{ m}^3$

$$T_1 = 273.15 + 27 = 300.15 \text{ K}$$

Using ideal gas equation, $pV = nRT$

$$\text{or } n = \frac{pV}{RT} = \frac{p_1 V_1}{RT_1} = \frac{16 \times 1.013 \times 10^5 \times 30 \times 10^{-3}}{8.314 \times 300.15}$$

$$= 19.48$$

$$\text{Final } p_2 = (11 + 1) = 12 \text{ atm} = 12 \times 1.013 \times 10^5 \text{ Pa}$$

$$V_2 = 30 \text{ L} = 30 \times 10^{-3} \text{ m}^3$$

$$T_2 = 273.15 + 17 = 290.15 \text{ K}$$

Number of moles

$$= \frac{p_2 V_2}{RT_2} = \frac{12 \times 1.013 \times 10^5 \times 30 \times 10^{-3}}{8.314 \times 290.15} = 15.12$$

$$\text{Hence, moles removed} = 19.48 - 15.12 = 4.36$$

$$\text{Mass removed} = 4.36 \times 32 \text{ g}$$

$$= 139.52 \text{ g} = 0.1395 \text{ kg}$$

LONG ANSWER Type II Questions

34. A gas in equilibrium has uniform density and pressure throughout its volume. This is strictly true only if there are no external influences. A gas column under gravity, e.g. does not have uniform density (and pressure). As you might expect, its density decreases with height. The precise dependence is given by the so called law of atmosphere.

$$n_2 = n_1 \exp[-mg(h_2 - h_1)/k_B T]$$

where, n_2 and n_1 refer to number density at heights h_2 and h_1 , respectively. Use this relation to derive the equation for sedimentation equilibrium of a suspension in a liquid column.

$$n_2 = n_1 \exp[-mg N_A (\rho - \rho')(h_2 - h_1)/(\rho RT)]$$

where, ρ is the density of the suspended particle and ρ' , that of surrounding medium.

$[\because N_A$ is Avogadro's number and R is the universal gas constant.] [NCERT]

Sol. According to the law of atmospheres,

$$n_2 = n_1 \exp\left[-\frac{mg}{k_B T} (h_2 - h_1)\right] \quad \dots(i)$$

where, n_2 and n_1 refer to number density of particles at heights h_2 and h_1 , respectively.

If we consider the sedimentation equilibrium of suspended particles in a liquid, then in place of mg , we will have to take effective weight of the suspended particles.

Let, V = average volume of a suspended particle,
 ρ = density of suspended particle, ρ' = density of liquid,
 m = mass of one suspended particle, m' = mass of equal volume of liquid displaced.

According to Archimedes' principle, effective weight of one suspended particle

$$= \text{Actual weight} - \text{weight of liquid displaced} = mg - m'g$$

$$= mg - V \rho' g = mg - \left(\frac{m}{\rho}\right) \rho' g = mg \left(1 - \frac{\rho'}{\rho}\right)$$

Also, Boltzmann constant, $k_B = \frac{R}{N_A}$

where, R is gas constant and N_A is Avogadro's number.

Putting, $mg \left(1 - \frac{\rho'}{\rho}\right)$ in place of mg and value of k_B in

Eq. (i), we get

$$n_2 = n_1 \exp \left[-\frac{mg N_A}{RT} \left(1 - \frac{\rho'}{\rho}\right) (h_2 - h_1) \right], \text{ which is required relation.}$$

- 35.** Given below are densities of some solids and liquids. Give rough estimate of the size of their atoms. [NCERT]

Substance	Atomic Mass (u)	Density ($10^{-3} \text{ kg m}^{-3}$)
(i) Carbon (diamond)	12.01	2.22
(ii) Gold	197.00	19.32
(iii) Nitrogen (liquid)	14.01	1.00
(iv) Lithium	6.94	0.53
(v) Fluorine (liquid)	19.00	1.14

Sol. We know, that, density of an element

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{\text{Mass of 1 mole}}{\text{Total volume of molecules in 1 mole when closely packed}}$$

$$\rho = \frac{M(\text{in grams})}{\left(\frac{4}{3}\pi r^3\right) N_A} = \frac{3 M \times 10^{-3} \text{ kg}}{4\pi r^3 \cdot N_A}$$

$$\Rightarrow r = \left[\frac{3 M \times 10^{-3}}{4\pi N_A \cdot \rho} \right]^{1/3}$$

where, N_A = Avogadro's number $\approx 6 \times 10^{23}$

(i) For carbon (diamond),

$$M = 12.01, \rho = 2.22 \times 10^3 \text{ kg/m}^3$$

$\therefore$ Radius of carbon atom

$$r = \left[\frac{3 \times 12.01 \times 10^{-3}}{4 \times 3.14 \times 6 \times 10^{23} \times 2.22 \times 10^3} \right]^{1/3}$$

$$= 1.29 \times 10^{-10} \text{ m}$$

$$= 1.29 \text{ \AA}$$

(ii) For gold, $M = 197.00, \rho = 19.32 \times 10^3 \text{ kg/m}^3$

$\therefore$ Radius of gold atom

$$r = \left[\frac{3 \times 197 \times 10^{-3}}{4 \times 3.14 \times 6 \times 10^{23} \times 19.32 \times 10^3} \right]^{1/3}$$

$$= 1.59 \times 10^{-10} \text{ m} = 1.59 \text{ \AA}$$

(iii) For nitrogen (liquid),

$$M = 14.01, \rho = 1.00 \times 10^3 \text{ kg/m}^3$$

$\therefore$ Radius of nitrogen atom

$$r = \left[\frac{3 \times 14.01 \times 10^{-3}}{4 \times 3.14 \times 6 \times 10^{23} \times 1.0 \times 10^3} \right]^{1/3}$$

$$= 1.77 \times 10^{-10} \text{ m} = 1.77 \text{ \AA}$$

(iv) For lithium, $M = 6.94, \rho = 0.53 \times 10^3 \text{ kg/m}^3$

$\therefore$ Radius of lithium atom

$$r = \left[\frac{3 \times 6.94 \times 10^{-3}}{4 \times 3.14 \times 6 \times 10^{23} \times 0.53 \times 10^3} \right]^{1/3}$$

$$= 1.73 \times 10^{-10} \text{ m} = 1.73 \text{ \AA}$$

(v) For fluorine (liquid),

$$M = 19.00 \text{ and } \rho = 1.14 \times 10^3 \text{ kg/m}^3$$

$\therefore$ Radius of fluorine atom

$$r = \left[\frac{3 \times 19.0 \times 10^{-3}}{4 \times 3.14 \times 6 \times 10^{23} \times 1.14 \times 10^3} \right]^{1/3}$$

$$= 1.88 \times 10^{-10} \text{ m} = 1.88 \text{ \AA}$$

- 36.** You are given, the following data about a group of particles, where n_i represents the number of molecules with speed v_i

n_i	2	4	8	6	3
$v_i (\text{ms}^{-1})$	1.0	2.0	3.0	4.0	5.0

- Calculate (i) average speed
(ii) rms speed
(iii) most probable speed.

Sol. (i) Average speed

$$= \frac{n_1 v_1 + n_2 v_2 + n_3 v_3 + n_4 v_4 + n_5 v_5}{n_1 + n_2 + n_3 + n_4 + n_5}$$

$$= \frac{2 \times 1 + 4 \times 2 + 8 \times 3 + 6 \times 4 + 3 \times 5}{2 + 4 + 8 + 6 + 3} = 3.17 \text{ m/s}$$

(ii) Root mean square speed

$$= \sqrt{\frac{n_1 v_1^2 + n_2 v_2^2 + n_3 v_3^2 + n_4 v_4^2 + n_5 v_5^2}{n_1 + n_2 + n_3 + n_4 + n_5}}$$

$$= \sqrt{\frac{2 \times 1^2 + 4 \times 2^2 + 8 \times 3^2 + 6 \times 4^2 + 3 \times 5^2}{2 + 4 + 8 + 6 + 3}}$$

$$= 3.36 \text{ m/s}$$

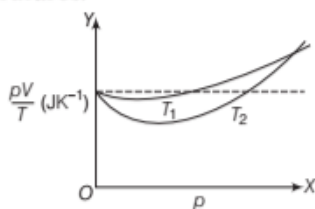
(iii) The most probable speed is that speed which is possessed by maximum number of molecules.

$$\text{Most probable speed } (v_{mp}) = \sqrt{\frac{2 k_B T}{m}} = \sqrt{\frac{3 k_B T}{m}} \times 2/3$$

$$v_{mp} = \sqrt{\frac{2}{3}} \times \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{2}{3}} v_{rms} = \sqrt{\frac{2}{3}} \times 3.36 \text{ m/s}$$

$$= 0.816 \times 3.36 \text{ m/s} = 2.74 \text{ m/s}$$

37. Figure shows plot of pV/T versus p for 1.00×10^{-3} kg of oxygen gas at two different temperatures.



[NCERT]

- What does the dotted plot signify?
- Which is true, $T_1 > T_2$ or $T_1 < T_2$?
- What is the value of pV/T , where the curves meet on the Y-axis?
- If we obtain similar plots for 1.00×10^{-3} kg of hydrogen, would we get the same value of pV/T at the point where the curves meet on the Y-axis? If not, what mass of hydrogen yields the same value of pV/T (for low pressure, high temperature region of the plot)? (Molecular mass of $H_2 = 2.02$ u, $O_2 = 32.0$ u, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$).

Sol. (i) Dotted plot shows that $\frac{pV}{T}$ is a constant quantity

$\left(\frac{pV}{T} = \mu R\right)$ which is independent of pressure. It signifies the ideal gas behaviour.

- As curve at temperature T_1 is closer to the dotted plot than the curve at temperature T_2 . Since, the behaviour of a real gas approaches the behaviour of perfect gas when temperature is increased, so $T_1 > T_2$.

- The value of $\frac{pV}{T}$, where the curves meet on Y-axis is

equal to μR .

Now, given mass of oxygen gas = 1.00×10^{-3} kg = 1 g

$$\therefore \frac{pV}{T} = \mu R = \left(\frac{1}{32}\right) \times 8.31 \text{ JK}^{-1}$$

$$= 0.26 \text{ JK}^{-1}$$

- If we use 1.00×10^{-3} kg of hydrogen, then we will not get same value of $\frac{pV}{T}$ at the point where the curves meet on Y-axis because molecular mass of hydrogen is different from oxygen.

Now, to get same value of $\frac{pV}{T}$, mass of hydrogen required is obtained from

$$\frac{pV}{T} = \mu R = \frac{m}{2.02} \times 8.31 = 0.26$$

$$\Rightarrow m = \frac{2.02 \times 0.26}{8.31} = 6.32 \times 10^{-2} \text{ g}$$

38. Consider an ideal gas with following distribution of speeds. [NCERT Exemplar]

Speed (m/s)	% of molecules
200	10
400	20
600	40
800	20
1000	10

- Calculate v_{rms} and hence T ($m = 3.0 \times 10^{-26}$ kg)
- If all the molecules with speed 1000 m/s escape from the system, calculate new v_{rms} and hence T .

Sol. This problem is designed to give an idea about cooling by evaporation

$$(i) v_{\text{rms}}^2 = \frac{\sum n_i v_i^2}{\sum n_i}$$

$$= \frac{10 \times (200)^2 + 20 \times (400)^2 + 40 \times (600)^2 + 20 \times (800)^2 + 10 \times (1000)^2}{100}$$

$$= \frac{10 \times 100^2 \times (1 \times 4 + 2 \times 16 + 4 \times 36 + 2 \times 64 + 1 \times 100)}{100}$$

$$= 1000 \times (4 + 32 + 144 + 128 + 100)$$

$$= 408 \times 1000 \text{ m}^2/\text{s}^2$$

$$\therefore v_{\text{rms}} = 639 \text{ m/s}$$

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

$$\therefore T = \frac{1}{3} \frac{m v_{\text{rms}}^2}{k}$$

$$= \frac{1}{3} \times \frac{3.0 \times 10^{-26} \times 4.08 \times 10^5}{1.38 \times 10^{-23}}$$

$$= 2.96 \times 10^2 = 296 \text{ K}$$

$$(ii) v_{\text{rms}}^2 = \frac{10 \times (200)^2 + 20 \times (400)^2 + 40 \times (600)^2 + 20 \times (800)^2}{90}$$

$$= \frac{10 \times 100^2 \times (1 \times 4 + 2 \times 16 + 4 \times 36 + 2 \times 64)}{90}$$

$$v_{\text{rms}}^2 = 10000 \times \frac{308}{9}$$

$$v_{\text{rms}}^2 = 342 \times 1000 \text{ m}^2/\text{s}^2$$

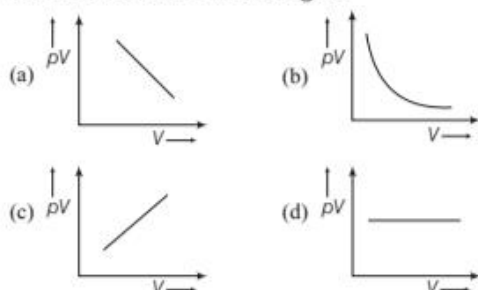
$$v_{\text{rms}} = 584 \text{ m/s}$$

$$T = \frac{1}{3} \frac{m v_{\text{rms}}^2}{k} = 248 \text{ K}$$

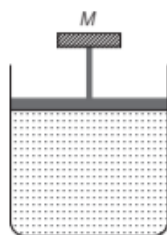
ASSESS YOUR TOPICAL UNDERSTANDING

OBJECTIVE Type Questions

- Which of the following options is correct about the flow of a liquid?
 - In liquids the atoms are not as rigidly fixed as in solid
 - In liquids the atoms are more rigidly fixed as in gas
 - In liquid the separation between atoms are spaced about $1 \text{ \AA}$
 - All of the above
- The mass of 22.4 L of any gas is equal to its molecular weight in grams at
 - 270 K and 1 atm
 - 273 K and 1 atm
 - 273 K and 10 atm
 - 270 K and 10 atm
- Which one of the following graphs represents the behaviour of an ideal gas?



- A cylinder containing an ideal gas is in vertical position and has a piston of mass M that is able to move up or down without friction (figure). If the temperature is increased [NCERT Exemplar]



- both p and V of the gas will change
 - only p will increase according to Charles' law
 - V will change but not p
 - p will change but not V
- Oxygen and hydrogen are at the same temperature T . The ratio of the mean kinetic energy of oxygen molecules to that of the hydrogen molecules will be
 - $16 : 1$
 - $1 : 1$
 - $4 : 1$
 - $1 : 4$

Answers

- (a)
- (b)
- (d)
- (c)
- (b)

VERY SHORT ANSWER Type Questions

- We have two different gases at the same temperature, then what will be the ratio of their average kinetic energies?
- If $4 : 9$ is ratio of densities of two gases at the given temperature. Find out the ratio of their rms speeds? [Ans. $3:2$]
- Draw temperature-volume graph of an ideal gas at constant pressure.
- What are the characteristics of gas molecules?
- State Boyle's law in terms of pressure and density.

SHORT ANSWER Type Questions

- Is it possible to increase the temperature of a gas while keeping its pressure and volume constant. Explain it?
- Draw p - V graph that shows the comparison of experimental and theoretical variations of p with V at constant temperature.
- The value of root mean square speed for O_2 is 400 m/s . Find the temperature of the O_2 . [Ans. $\approx 200 \text{ K}$]
- If value of most probable speed for an ideal gas is 500 m/s . Find the value of root mean square speed for this gas. [Ans. 390 m/s]
- Find the temperature at which rms speed of a gas is half of its value of 0°C , pressure remaining constant. [Ans. 68.25 K]

LONG ANSWER Type I Questions

- Write the assumptions of kinetic theory of gases.
- Find the expression for the average kinetic energy of a molecule of an ideal gas.
- At what temperature, will the molecules in a sample of helium gas have an rms speed of 1.0 km/s ? [Ans. 160 K]
- If the pressure of a gas filled in closed container is increased by 0.2% . When temperature is increased by 1 K , calculate the initial temperature of the gas. [Ans. 500 K]

20. If the ratio of molecular weights of two gases is 4. What will be ratio of the v_{rms} values for the molecules of those two gases? [Ans. 0.5]

LONG ANSWER Type II Questions

21. A box of 1.00 m^3 is filled with nitrogen at 1.5 atm at 300 K. The box has a hole of an area 0.010 mm^2 . How much time is required for the pressure to reduce by 0.10 atm, if the pressure outside is 1 atm. [Ans. $1.38 \times 10^5 \text{ s}$]
22. An oxygen cylinder of volume 30 L has an initial gauge pressure of 15 atm and a temperature of 27°C .

After some oxygen is withdrawn from the cylinder, the gauge pressure drop to 11 atm and its temperature drops to 17°C . Estimate mass of oxygen taken out of the cylinder ($R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$, molecular mass of $\text{O}_2 = 32$) [Ans. 141 g]

23. An electric bulb of volume 250 cm^3 was sealed off during manufacture at a pressure of 10^{-3} mm of mercury at 27°C .

Compute the number of air molecules contained in the bulb.

Given that, $R = 8.31 \text{ J/mol/K}$
and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$.

[Ans. 8×10^{15}]

|TOPIC 2|

Motion of Gas Molecules

DEGREE OF FREEDOM

The total number of coordinates or independent quantities required to describe completely the position and configuration of a dynamical system is known as number of **degrees of freedom** of the system. It is represented by f and expressed as

Degree of freedom, $f = 3N - K$

where, N is the number of particles in a system and K is number of independent relations between the particles.

- (i) In case of monoatomic gas, such as helium, neon argon, have translational degree of freedom.

If $N = 1$ and $K = 0$, then $f = 3 \times 1 - 0 = 3$

- (ii) In case of diatomic gas, such as oxygen, hydrogen, nitrogen etc., each molecule has two rotational degrees of freedom in addition to three translational degrees of freedom.

$\therefore f = 5$

- (iii) The gas like SO_2 , H_2S etc., has three molecules, i.e. they are triatomic gases. In case of triatomic gases,

$f = 7$ for linear molecules

and $f = 6$ for non-linear molecules

LAW OF EQUIPARTITION OF ENERGY

It states that

'For a dynamic system in thermal equilibrium, the total energy is distributed equally amongst all the degree of freedom and the energy associated with each molecule per degree of freedom is $\frac{1}{2} k_B T$.'

Where, $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$ is Boltzmann constant and T is absolute temperature of system on the kelvin scale. For a monoatomic gas in thermal equilibrium at temperature T , the average value of translational energy of the molecule is

$$\langle E_t \rangle = \left\langle \frac{1}{2} m v_x^2 \right\rangle + \left\langle \frac{1}{2} m v_y^2 \right\rangle + \left\langle \frac{1}{2} m v_z^2 \right\rangle$$

Translational energy of the molecules, $\langle E_t \rangle = \frac{3}{2} k_B T$

Since, there is no preferred direction, then the above equation can be written as

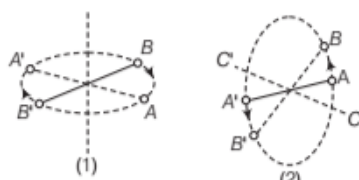
$$\left\langle \frac{1}{2} m v_x^2 \right\rangle = \frac{1}{2} k_B T, \left\langle \frac{1}{2} m v_y^2 \right\rangle = \frac{1}{2} k_B T, \left\langle \frac{1}{2} m v_z^2 \right\rangle = \frac{1}{2} k_B T$$

Thus, energy associated with each molecule per degree of freedom is $\frac{1}{2}k_B T$, which is law of equipartition of energy.

Therefore, total energy of a diatomic gas molecule is the sum of translational energy E_t and rotational energy E_r ,

$$E_t + E_r = \left(\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \right) + \left(\frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 \right)$$

where, ω_1 and ω_2 are angular speeds about the axes 1 and 2 and I_1 and I_2 are moment of inertia.



Rotation of a diatomic molecule

In case of diatomic/polyatomic gas, molecules may not be a **rigid rotator** having no vibration. Molecules like CO at moderate temperatures have a mode of vibration and contributes a vibrational energy E_v to total energy

$$E_v = \frac{1}{2}m\left(\frac{dy}{dt}\right)^2 + \frac{1}{2}ky^2$$

where, k = force constant of the oscillator

and y = vibrational coordinate

$\therefore$ Total energy, $E = E_t + E_r + E_v$

SPECIFIC HEAT CAPACITY (C)

In this topic, we will deal with the specific heat capacity of gases having different degree of freedom. It can be calculated by applying the law of equipartition of energy of gases.

Monoatomic Gases

In monoatomic gases, a molecule has three translational degrees of freedom. By law of equipartition of energy, average energy per molecule per degree of freedom $= \frac{1}{2}k_B T$.

So, average energy per molecule with three degrees of freedom $= 3 \times \frac{1}{2}k_B T = \frac{3}{2}k_B T$

Now, total internal energy of one mole of monoatomic gas

$$U = \frac{3}{2}k_B T \times N_A = \frac{3}{2}RT \quad (\text{as } R = N_A k_B)$$

$$\therefore U = \frac{3}{2}RT \quad \dots(i) \quad [\text{for monoatomic gas}]$$

If dU is a small amount of heat energy required to raise the temperature of 1g mole of the gas at constant volume through at temperature dT . Then,

$$C_V = \frac{dU}{dT} \quad [\because \mu = 1] \dots(ii)$$

where, C_V = specific heat of gas at constant volume.

Putting, $U = \frac{3}{2}RT$ in Eq. (ii), we have

$$C_V = \frac{d}{dT} \left(\frac{3}{2}RT \right) = \frac{3}{2}R$$

$$\therefore C_V = \frac{3}{2}R$$

If C_p is molar specific heat at constant pressure, then

$$C_p - C_V = R$$

$$\Rightarrow C_p - \frac{3}{2}R = R$$

$$\therefore C_p = \frac{5}{2}R$$

$$\text{Now, ratio of specific heat, } \gamma = \frac{C_p}{C_V} = \frac{\left(\frac{5}{2}\right)R}{\left(\frac{3}{2}\right)R} = \frac{5}{3} = 1.67$$

Ratio of specific heat capacities for monoatomic gases

$$\gamma = 1.67$$

EXAMPLE [1] Kinetic Energy in Helium Atom

Calculate the molecular kinetic energy of 1 g of helium (molecular weight 4) at 127°C . (Given, $R = 8.31 \text{ Jmol}^{-1}\text{K}^{-1}$)

Sol. Given, $T = 273 + 127 = 400 \text{ K}$

Helium is monoatomic gas.

$$\therefore \text{Average kinetic energy per mole of helium} = \frac{3}{2}RT$$

Average kinetic energy of 1 g of helium

$$= \frac{3}{2} \frac{RT}{M} = \frac{3 \times 8.31 \times 400}{2 \times 4} = 1246.5 \text{ J}$$

Diatomic Gases

In case of diatomic gases, if the vibrational mode is not considered, then it has five degrees of freedom (three translational and two rotational) at room temperature.

According to law of equipartition of energy, total internal energy of one mole of such type of gas is

$$U = 5 \times \left(\frac{1}{2}k_B T \right) \times N_A$$

$$\text{Thus, } U = \frac{5}{2}RT \quad [\because R = k_B N_A]$$

The molar specific heat C_V is given by,

$$\text{So, } C_V = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{5}{2} RT \right)$$

$$\therefore C_V = \frac{5}{2} R$$

$$\text{Now, } C_p = C_V + R \Rightarrow C_p = \frac{5}{2} R + R = \frac{7}{2} R$$

$$\text{So, } C_p = \frac{7}{2} R$$

$$\text{So, } \gamma = \frac{C_p}{C_V} = \frac{\left(\frac{7}{2}\right)R}{\left(\frac{5}{2}\right)R} \Rightarrow \gamma = \frac{7}{5} = 1.40$$

Ratio of specific heat capacities for diatomic gases

$$\gamma = 1.40$$

EXAMPLE [2] Diatomic Gas Molecule

Calculate the total number of degrees of freedom possessed by the molecules in 1 cm^3 of H_2 gas at temperature 273 K

and 1 atm pressure? [NCERT Exemplar]

Sol. At 273 K temperature and 1 atm pressure mean STP condition.

$$\therefore \text{Number of } \text{H}_2 \text{ molecules on } 22400 \text{ cm}^3 \text{ at STP} \\ = 6.02 \times 10^{23}$$

$$\therefore \text{Number of } \text{H}_2 \text{ molecules in } 1 \text{ cm}^3 \text{ at STP}$$

$$= \frac{6.02 \times 10^{23}}{22400} = 2.6875 \times 10^{19}$$

Number of degrees of freedom associated with each H_2 (diatomic) molecule = 5

$$\therefore \text{Total number of degrees of freedom associated with } 1 \text{ cm}^3 \text{ of gas} = 2.6875 \times 10^{19} \times 5 = 1.34375 \times 10^{20}$$

EXAMPLE [3] Specific Heat at Constant Volume

Find the value of internal energy of one mole of a diatomic gas, which do not show vibrational mode. Also, find the value of C_V for the sample of above gas.

Sol. Molecule of diatomic gas will have three translational and two rotational degrees of freedom. So,

$$\text{Degrees of freedom } (f) = 3 + 2 = 5$$

$$\text{Total energy } (E) = 5 \left(\frac{1}{2} k_B T \right) = \frac{5}{2} k_B T$$

As the gas is one mole, so the total number of molecules is N_A . So, total energy of one mole of gas could be found.

$$U = \frac{5}{2} k_B T \times N_A = \frac{5}{2} k_B N_A T = \frac{5}{2} RT$$

We can find the value of C_V by applying, $C_V = \frac{dU}{dT}$

$$C_V = \frac{d}{dT} \left(\frac{5}{2} RT \right) \Rightarrow C_V = \frac{5}{2} R$$

Triatomic Gas

In case of such kind of gases (linear triatomic gas), there are seven degrees of freedom. Using law of equipartition of energy, total internal energy of one mole of such gases is

$$U = 7 \times \left(\frac{1}{2} k_B T \right) \times N_A = \frac{7}{2} RT [\because k = k_A N_B]$$

$$\text{Now, } C_V = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{7}{2} RT \right) = \frac{7}{2} R$$

$$\Rightarrow C_V = \frac{7}{2} R$$

$$\text{Now, } C_p = C_V + R = \frac{7}{2} R + R \Rightarrow C_p = \frac{9}{2} R$$

$$\therefore \gamma = \frac{C_p}{C_V} = \frac{\left(\frac{9}{2}\right)R}{\left(\frac{7}{2}\right)R} = \frac{9}{7}$$

$$\Rightarrow \gamma = \frac{9}{7} = 1.28$$

Ratio of specific heat capacities for triatomic gases,

$$\gamma = 1.28$$

Polyatomic Gas

A polyatomic gas molecule in general has three translational, three rotational degrees of freedom and with certain number (let f) of vibrational modes.

Using law of equipartition of energy, total internal energy of one mole of such gases is

$$U = \left[\frac{3}{2} k_B T + \frac{3}{2} k_B T + f k_B T \right] \times N_A$$

$$\Rightarrow U = (3 + f) RT$$

$$\text{Now, } C_V = \frac{dU}{dT} \\ = \frac{d(3 + f) RT}{dT} = (3 + f) R$$

$$\Rightarrow C_V = (3 + f) R$$

$$\therefore C_p = C_V + R = (3 + f) R + R$$

$$\Rightarrow C_p = (4 + f) R$$

$$\text{So, } \gamma = \frac{C_p}{C_V} = \frac{(4 + f)}{(3 + f)}$$

$$\text{Taking } f = 6$$

Ratio of specific heat capacities for polyatomic gas, $\gamma = 1.11$

Determination of γ from the Degrees of Freedom

If a polyatomic gas molecule has f degrees of freedom, then internal energy of one mole of the gas is

$$U = f \times \left(\frac{1}{2} k_B T \right) \times N_A = \frac{f}{2} RT$$

Now,

$$C_V = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{f}{2} RT \right) = \frac{f}{2} R$$

$$C_V = \frac{f}{2} R$$

$$\therefore C_P = C_V + R = \frac{f}{2} R + R = \left(\frac{f}{2} + 1 \right) R$$

$$C_P = \left(\frac{f}{2} + 1 \right) R$$

So, specific heat ratio is

$$\gamma = \frac{C_P}{C_V} = \frac{\left(\frac{f}{2} + 1 \right) R}{\frac{f}{2} R}$$

$$\Rightarrow \gamma = \left(1 + \frac{2}{f} \right)$$

which is required relation between γ and f .

EXAMPLE [4] An Isolated Container

An isolated container containing monoatomic gas of molar mass m is moving with a velocity v_0 . If the container is suddenly stopped, find the change in temperature.

[NCERT Exemplar]

Sol. Loss in kinetic energy of gas $= \Delta E = \frac{1}{2} (mn) v_0^2$

where, n is number of moles and m is molar mass.

If its temperature changes by ΔT , then

$$\frac{3}{2} n R \Delta T = \frac{1}{2} mn v_0^2$$

$$\therefore \text{Change in temperature, } \Delta T = \frac{mv_0^2}{3R}$$

Specific Heat Capacity of Solids

In solids, each atom vibrates about its mean position, let us consider one mole of solid containing N_A atoms. By law of equipartition of energy, average energy associated with an atom due to its oscillation in one dimension is

$$= 2 \times \left(\frac{1}{2} k_B T \right) = k_B T$$

$\therefore$ In three dimension (3D) average energy per atom $= 3 k_B T$.

$\therefore$ Total energy of one mole of solid is

$$U = (3 k_B T) \times N_A = 3 RT \quad [\because k_B N_A = R]$$

According to first law of thermodynamics

$$\Delta Q = \Delta U + \Delta W \quad \text{or} \quad \Delta Q = \Delta U + p \Delta V$$

In case of solid, ΔV is negligible

$$\therefore \Delta Q = \Delta U$$

$$\text{Molar specific heat of solid, } C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T}$$

Specific heat capacity of solids, $C = 3R$

$$\Rightarrow C = 24.93 \text{ J mol}^{-1} \text{K}^{-1} \quad [\because R = 8.31 \text{ J mol}^{-1} \text{K}^{-1}]$$

Specific Heat Capacities of Some Solids at Room Temperature and Atmospheric Pressure

Substance	Specific Heat (J kg ⁻¹ K ⁻¹)	Molar Specific Heat (J mol ⁻¹ K ⁻¹)
Aluminium	900.0	24.4
Carbon	506.5	6.1
Copper	386.4	24.5
Lead	127.7	26.5
Silver	236.1	25.5
Tungsten	134.4	24.9

From this table, it is clear that the prediction generally agrees with experimental values at ordinary temperature except i.e. carbon.

Note

The temperature at which all metals have constant C_V is called **Debye temperature**.

Specific Heat Capacity of Water

If we consider water molecule as a solid made up of 3 atoms (2 hydrogen and 1 oxygen) and each atom is free to vibrate in three dimensions about its mean position.

By using law of equipartition of energy, average energy associated with one atom of water molecule

$$= 2 \times \left(\frac{1}{2} k_B T \right) = k_B T$$

In three dimension, the average energy per atom of water molecule $= 3 k_B T$

$\therefore$ Total energy of one molecule of water is

$$= 3 \times (3 k_B T) = 9 k_B T$$

Now, total energy of 1 mole of water is

$$U = 3 \times 3 k_B T \times N_A = 9 RT$$

$\therefore$ Molar specific heat of water,

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 9R$$

Specific heat capacity of water, $C = 9R$
 $\Rightarrow C = 74.79 \text{ J mol}^{-1} \text{ K}^{-1}$
 $[\because R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}]$

EXAMPLE [5] A Mixture of Gases

A gas mixture consists of 2.0 moles of oxygen and 4.0 moles of neon at temperature T . Neglecting all vibrational modes, calculate the total internal energy of the system. (oxygen has two rotational modes) [NCERT Exemplar]

Sol. O_2 has five degrees of freedom.

Therefore, energy per mole = $\frac{5}{2}RT$

$\therefore$ For 2 moles of O_2 , energy = $5RT$

Neon has three degrees of freedom

$\therefore$ Energy per mole = $\frac{3}{2}RT$

$\therefore$ For 4 moles of neon, energy

$= 4 \times \frac{3}{2}RT = 6RT$

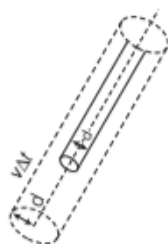
$\therefore$ Total energy = $5RT + 6RT = 11RT$.

MEAN FREE PATH (λ)

Every gas consists of a large number of molecules undergoing frequent collision, therefore they cannot move straight or unhindered, these molecules are in a state of continuous and random motion. Also, they undergo perfectly elastic collision against each other. The average distance travelled by a molecule between two successive collisions is known as the **mean free path of the molecule**.

Expression for Mean Free Path

Let d be the diameter of each molecule of the gas, then a particular molecule will suffer collision with any molecule that comes within a distance d between centres of two molecules.



Volume swept by a molecule in time Δt

If $\bar{v}$ is average speed of molecule, then from figure, the volume swept by the molecule in small time Δt in which any molecule will collide with it

$$= \pi d^2 \langle v \rangle \Delta t$$

If n is number of molecules per unit volume of the gas, then number of collision suffered by the molecule in time Δt

$$= \pi d^2 \langle v \rangle \Delta t \times n.$$

So, number of collisions per second

$$= \frac{\pi d^2 \langle v \rangle \Delta t \times n}{\Delta t} = n \pi d^2 \langle v \rangle$$

$\therefore$ Average time between two successive collisions

i.e. $\tau = \frac{1}{n \pi d^2 \langle v \rangle}$

$\therefore$ Mean free path = average distance between two successive collision

$$\Rightarrow \lambda = \tau \times \text{mean velocity} = \frac{1}{n \pi d^2 \langle v \rangle} \times \bar{v} = \frac{1}{n \pi d^2}$$

Mean free path, $\lambda = \frac{1}{n \pi d^2}$

where, d = diameter of each molecule

and n = number of molecules per unit volume.

Basic Assumptions on Mean Free Path

- (i) The molecules of gas are considered as hard spheres, each of diameter d .
- (ii) The collision between gas molecules are perfectly elastic.
- (iii) All molecules of a gas except the molecule under consideration are at rest.
- (iv) A molecule of the gas under consideration collides with all those molecules whose centre are at distance d from centre of molecule under consideration.

In the above derivation of λ , we imagined the other molecules to be at rest. But actually all molecules are moving, which will result into the following more accurate value.

$$\lambda = \frac{1}{\sqrt{2} n \pi d^2} \quad \dots(i)$$

where, T = temperature of gas (in kelvin),

d = molecules diameter

and λ = mean free path.

Note

Mean free path, $\lambda = \frac{K_B T}{\sqrt{2} \pi d^2 P}$ (in terms of temperature and pressure)

- The mean free path of a given gas is (i) directly proportional to its absolute temperature, and (ii) inversely proportional to its pressure.
- Using kinetic theory of gases, the Bulk measurable properties like viscosity, heat conductivity and rate of diffusion are easily related to the microscopic parameters like molecular size.

EXAMPLE [6] Flying with Planes

Ten small planes are flying at a speed of 150 km/h in total darkness in an air space that is $20 \times 20 \times 1.5 \text{ km}^3$ in volume. You are in one of the planes, flying at random within this space with no way of knowing where the other planes are. On the average about how long a time will elapse between near collision with your plane. Assume for this rough computation that a safety region around the plane can be approximated by a sphere of radius 10 m. [NCERT Exemplar]

Sol. Given, $v = 150 \text{ km/h}$, $V = 20 \times 20 \times 1.5$,

$$N = 10, \quad d = 2 \times 10 = 20 \text{ m}$$

Time taken by plane, $t = \lambda/v$ and mean free path

$$\text{i.e.} \quad \lambda = \frac{1}{\sqrt{2} n d^2}$$

where, d = diameter and n = number of density

$$\text{So,} \quad n = \frac{N}{V} = \frac{10}{20 \times 20 \times 1.5} = 0.0167 \text{ km}^{-3}$$

and time elapse between collision,

$$t = \frac{1}{\sqrt{2} n d^2 (N/V) \times v} \\ = \frac{1}{1.414 \times 3.14 \times (20)^2 \times 0.0167 \times 10^{-3} \times 150} = 0.225 \text{ h}$$

EXAMPLE [7] Mean Free Path

The average speed of air molecules is 485 m/s. At STP the number density is $2.7 \times 10^{25} / \text{m}^3$ and diameter of the air molecule is $2 \times 10^{-10} \text{ m}$. Find the value of mean free path (λ) for the air molecule and average time (τ) between successive collisions.

Sol. To find the mean free path, we need the values of d and n . Just put these values in the formula of mean free path.

$$\lambda = \frac{1}{\sqrt{2} n \pi d^2} = \frac{1}{\sqrt{2} \pi \times 2.7 \times 10^{25} (2 \times 10^{-10})^2} \\ = 2.9 \times 10^{-7} \text{ m}$$

$$\text{The value of } \tau = \frac{l}{v}$$

Now, put the values and get the value of τ .

$$\tau = \frac{2.9 \times 10^{-7}}{485} = 5.9 \times 10^{-10} \text{ s}$$

BROWNIAN MOTION

In 1827, a Scottish Botanist, Robert Brown saw the pollen grains moving continuously in *zig-zag* random motion while observing the pollen grains of a flower under a microscope. Brownian motion is the *zig-zag motion* of the particles of microscope of size suspended in water, air or some other fluid. This motion can be explained on the basis of kinetic theory.

A very small particle (of the order of 10^{-5} m) suspended in a fluid is continuously bombarded from all sides by the molecules of the fluid. The impulses and the torque acting on the suspended particle due to continuous bombardment do not sum to zero exactly, therefore, a net torque or impulse in one or the other direction exists. It is due to the net torque that the suspended particle moves continuously in a random motion.

The Brownian motion depends upon the following factors as

- (i) Size of the suspended particle
- (ii) Density of the fluid
- (iii) Temperature of the medium
- (iv) Viscosity of the medium

In 1987, Ahmed Zewall, an Egyptian scientist observed the detailed interactions by illuminating them with flashes of laser light for very short duration of order 10 femto seconds ($1 \text{ femto-second} = 10^{-15} \text{ s}$).

TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. The average energy associated with each translational degree of freedom is

- (a) $\frac{3}{2} k_B T$ (b) $k_B T$
(c) $\frac{1}{2} k_B T$ (d) $2k_B T$

Sol. (c) Average energy associated with each translational degree of freedom is $\frac{1}{2} k_B T$.

2. Diatomic molecule (rigid rotator) has

- (a) 3 translational degrees of freedom
(b) 2 rotational degrees of freedom
(c) Both (a) and (b)
(d) All of the above

Sol. (c) The diatomic molecules (without vibrational mode) like O_2 and N_2 has three translational degrees of freedom and two rotational degrees of freedom.

3. Law of equipartition of energy is used to

- (a) predict the specific heats of gases
(b) predict the specific heats of solids
(c) Both (a) and (b)
(d) Neither (a) nor (b)

Sol. (c) Law of equipartition of energy is used to predict the specific heat of gases and solids.

4. The internal energy of 2 moles of a monoatomic gas is

(a) $\frac{3}{2} RT$ (b) $3 RT$ (c) $2 RT$ (d) $5 RT$

Sol. (b) Internal energy, $U = \left(\frac{3}{2} k_B T\right) 2N_A$
 $= 3 (k_B \times N_A) T = 3 RT.$

5. The mean free path for air molecule with average speed 18.5 ms^{-1} at STP is
 (Take, $d = 2 \times 10^{-10} \text{ m}$ and $n = 2.7 \times 10^{25} \text{ m}^{-3}$)

(a) $3.5 \times 10^{-7} \text{ m}$ (b) $4 \times 10^{-7} \text{ m}$
 (c) $2.9 \times 10^{-7} \text{ m}$ (d) $5 \times 10^{-7} \text{ m}$

Sol. (c) For air at STP, $n = 2.7 \times 10^{25} \text{ m}^{-3}$

$$d = 2 \times 10^{-10} \text{ m}$$

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

On putting values, $l = 2.9 \times 10^{-7} \text{ m}$

VERY SHORT ANSWER Type Questions

6. What is the number of degree of freedom of a bee flying in a room?

Sol. Three, because bee is free to move along x-direction or y-direction or z-direction.

7. How degree of freedom of a gas molecule is related with the temperature?

Sol. Degree of freedom will increase when temperature is very high because at high temperature, vibrational motion of the gas will contribute to the kinetic energy. Hence, there is an additional kinetic energy associated with the gas, as a result of increased degree of freedom.

8. Is molar specific heat of a solid, a constant quantity?

Sol. Yes, the molar specific heat of a solid is a constant quantity as its value is $3R \text{ J/mol}^{-1} \text{ K}^{-1}$.

9. The specific heat of argon at constant volume is $0.075 \text{ kcal kg}^{-1} \text{ K}^{-1}$, then what will be its atomic weight? [Given, $R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$]

Sol. Argon is a monoatomic gas, so

$$C_V = \frac{3}{2} R = \frac{3}{2} \times 2 = 3 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$C_V = M c_V$$

$$\Rightarrow M = \frac{C_V}{c_V} = \frac{3}{0.075} = 40$$

10. Name an experimental evidence in support of random motion of gas molecules.

Sol. Brownian motion and diffusion of gases provide experimental evidence in support of random motion of gas molecules.

11. What is mean free path of a gas?

Sol. The average distance travelled by a molecule between two successive collisions is known as mean free path of the molecule.

12. How is mean free path depends on number density of the gas?

Sol. The mean free path is inversely proportional to the number density of the gas.

13. Calculate the ratio of the mean free paths of the molecules of two gases having molecular diameters $1 \text{ \AA}$ and $2 \text{ \AA}$. The gases may be considered under identical conditions of temperature, pressure and volume.

[NCERT Exemplar]

Sol. As, we know, mean free path, $\lambda \propto \frac{1}{d^2}$

Given, $d_1 = 1 \text{ \AA}$ and $d_2 = 2 \text{ \AA}$

$$\Rightarrow \lambda_1 : \lambda_2 = 4 : 1$$

14. If a molecule having N atoms has k number of constraints, how many degrees of freedom does the gas possess?

Sol. Degree of freedom, $f = 3N - K$.

15. If there are f degrees of freedom with n moles of a gas, then find the internal energy possessed at a temperature T .

Sol. For 1 mole with f degrees of freedom,

$$\text{Internal energy, } U = 1 \times C_V \times T = \frac{f}{2} RT$$

For n moles, $U = n C_V T = \frac{nf}{2} RT$

SHORT ANSWER Type Questions

16. Equal masses of monoatomic and diatomic gases are supplied heat at the same temperature, pressure and volume.

If same amount of heat is supplied to both the gases, which of them will undergo greater temperature rise?

Sol. For monoatomic gas, temperature rise will be greater because monoatomic gas possesses only translational degree of freedom whereas diatomic gas translation, rotation and vibrational (at higher temperature), so temperature rise for diatomic gases is lower.

17. At room temperature, diatomic gas molecule has five degrees of freedom, at high temperature. It has seven degrees of freedom, explain?

Sol. At low temperature, diatomic gas has three translational and two rotational degrees of freedom, so total number of degrees of freedom is 5.

But at high temperature, gas molecule starts to vibrate which give two additional degrees of freedom i.e. 7.

- 18.** Calculate the number of degrees of freedom in 15 cm^3 of nitrogen at NTP.

Sol. Number of nitrogen molecules in 22400 cm^3 of gas at NTP = 6.023×10^{23}

$$\therefore \text{Number of nitrogen molecules in } 15 \text{ cm}^3 \text{ of gas at NTP} \\ = \frac{6.023 \times 10^{23} \times 15}{22400} = 4.03 \times 10^{20}$$

Number of degrees of freedom of nitrogen (diatomic) molecule at $273 \text{ K} = 5$

$$\therefore \text{Total degrees of freedom of } 15 \text{ cm}^3 \text{ of gas} \\ = 4.03 \times 10^{20} \times 5 \\ = 2.015 \times 10^{21}$$

- 19.** A diatomic gas is heated in a vessel to a temperature of 10000 K . If each molecule possess an average energy E_1 . After sometime, a few molecule escape into the atmosphere at 300 K . Due to which, their energy changes to E_2 . Calculate the ratio of $\frac{E_1}{E_2}$.

Sol. Number of degrees of freedom of diatomic gas at $10000 \text{ K} = 7$.

Number of degrees of freedom of diatomic gas at $300 \text{ K} = 5$

$$\therefore \frac{E_1}{E_2} = \frac{\left(\frac{7}{2}\right) k_B T_1}{\left(\frac{5}{2}\right) k_B T_2} = \frac{7}{5} \times \frac{T_1}{T_2} = \frac{7}{5} \times \frac{10000}{300} = \frac{140}{3}$$

- 20.** What will be the internal energy of 8 g of oxygen at STP?

Sol. Oxygen is a diatomic gas.

Number of moles of O_2 gas

$$= \frac{\text{Atomic wt.}}{\text{Molecular wt.}} = \frac{8}{32} \\ = \frac{1}{4} = 0.25$$

$\therefore$ Energy associated with 1 mole of oxygen

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

$\therefore$ Internal energy of 8 g of oxygen

$$= 0.25 \times \frac{5}{2} RT \\ = 0.25 \times \frac{5}{2} \times 8.31 \times 273 = 1417.9 \text{ J}$$

- 21.** Give a formula for mean free path of the molecules of a gas. Briefly explain, how its value is affected by (i) change in temperature and (ii) change in pressure.

Sol. As, we know that the value of mean free path of the molecules of a given gas is given by

$$\text{Mean free path, } \lambda = \frac{1}{\sqrt{2} n d^2}$$

Here, n = number of gas molecules present in unit volume of given gas and d = molecular diameter.

- (i) **Effect of temperature** As temperature of a gas is increased at constant pressure, volume of gas increases and hence n , the number of molecules per unit volume decrease. In fact

$$n \propto \frac{1}{V} \text{ and } V \propto T,$$

$$\text{Thus, } n \propto \frac{1}{T}$$

Due to decrease in molecular number density, the value of mean free path of the gas increase i.e.

$\lambda \propto \frac{1}{n} \propto T$. Thus, pressure remaining constant, the mean free path of a gas is directly proportional to its absolute temperature.

- (ii) **Effect of pressure** At constant temperature, on increasing pressure, the volume V decrease, the molecular number density n increases and consequently, the mean free path decreases

$$\text{i.e. } p \propto \frac{1}{V} \propto n$$

$$\therefore \lambda \propto \frac{1}{n}$$

$$\text{or } \lambda \propto \frac{1}{p}$$

Thus, at a constant temperature, the mean free path of a gas is inversely proportional to its pressure.

- 22.** What is basic law followed by equipartition of energy?

Sol. The law of equipartition of energy for any dynamical system in thermal equilibrium, the total energy is distributed equally amongst all the degrees of freedom.

The energy associated with each molecule per degree of freedom is $\frac{1}{2} k_B T$, where k_B is Boltzmann's constant and T is temperature of the system.

- 23.** Explain qualitatively, how the extent of Brownian motion is affected by the

- size of the Brownian particle,
- density of the medium,
- temperature of the medium,
- viscosity of the medium?

[NCERT]

Sol. The effect of the various factors on the Brownian motion is as follows

Factors	Effects
(a) Decrease in the size of the Brownian particle.	Increase of Brownian motion.
(b) Decrease in the density of the medium.	Increase of Brownian motion.
(c) Increase in temperature of the medium.	Increase of Brownian motion.
(d) Increase in viscosity of the medium.	Decrease of Brownian motion.

24. Calculate the mean free path of a molecule of a gas at a room temperature and one atmospheric pressure. The radius of the gas molecules (avg) is 2×10^{-10} m?

Sol. Given, $T = 27^\circ\text{C} = 273 + 27 = 300\text{ K}$,
 $P = 1\text{ atm} = 1.01 \times 10^5\text{ N/m}^2$
 $d = 2 \times 2 \times 10^{-10}\text{ m} = 4 \times 10^{-10}\text{ m}$
 $\therefore$ Mean free path, $\lambda = \frac{K_B T}{\sqrt{2} \pi d^2 p}$

$$= \frac{1.38 \times 10^{-23} \times 300}{1.414 \times 3.14 (4 \times 10^{-10})^2 \times 1.013 \times 10^5}$$

$$= 5.75 \times 10^{-8}\text{ m}$$

25. Although velocity of air molecules is very fast but fragrance of a perfume spreads at a much slower rate, explain?

Sol. This is because scent vapour molecules do not travel uninterrupted, they undergo a number of collisions and trace a zig-zag path, due to which their effective displacement per unit time is small, so spreading is at a much slower rate.

LONG ANSWER Type I Questions

26. Calculate the temperature atoms at which rms speed of Argon gas is equal to the rms speed of Helium gas atoms at -10°C ? (Atomic mass of Ar = 39.9 u, that of He = 4u)

Sol. As we know that, $V_{\text{rms}} = \sqrt{\frac{3RT}{M}}$
 Thus, $V_{\text{rms}} / \text{Ar} = V_{\text{rms}} / \text{He}$

$$\Rightarrow \sqrt{\frac{T_{\text{Ar}}}{M_{\text{Ar}}}} = \sqrt{\frac{T_{\text{He}}}{M_{\text{He}}}}$$

 $T_{\text{Ar}} = ? \quad T_{\text{He}} = 273 - 10 = 263\text{ K}$
 $M_{\text{Ar}} = 39.9\text{ u}, M_{\text{He}} = 4\text{ u}$
 Thus,
$$\frac{T_{\text{Ar}}}{39.9} = \frac{263}{4}$$

$$T_{\text{Ar}} = \frac{263 \times 39.9}{4} = 2623.43\text{ K}$$

27. If one mole of a monoatomic gas is mixed with three moles of a diatomic gas. What is the molar specific heat of mixture at constant value? [Take, $R = 8.31\text{ J mol}^{-1}\text{K}^{-1}$]

Sol. Given, for monoatomic gas, $\mu_1 = 1$, $C_{V_1} = \frac{3}{2}R$ and for a

diatomic gas, $\mu_2 = 3$ and $C_{V_2} = \frac{5}{2}R$

$\therefore$ Total heat energy required to raise the temperature of mixture by ΔT .

$$\Delta U = \mu_1 C_{V_1} \Delta T + \mu_2 C_{V_2} \Delta T$$

$$\Delta U = 1 \times \frac{3}{2} R \Delta T + 3 \times \frac{5}{2} R \Delta T = 9R\Delta T \quad \dots(i)$$

Let C_{V_m} be the molar specific heat of the mixture at constant volume and as total number of moles of mixture.

$$\mu_m = 1 + 3 = 4$$

$\therefore$ Heat energy required

$$\Delta U = \mu_m C_{V_m} \Delta T$$

$$\Rightarrow \Delta U = 4 C_{V_m} \Delta T \quad \dots(ii)$$

From Eqs. (i) and (ii), we have

$$9R\Delta T = 4 C_{V_m} \Delta T$$

$$\Rightarrow \Delta C_{V_m} = \frac{9}{4} R = 2.25 R$$

28. A cylinder of fixed capacity contains 44.8 L of helium gas at STP. Calculate the amount of heat required to raise the temperature of container by 15°C ?

[given $R = 8.31\text{ J mol}^{-1}\text{K}^{-1}$]

Sol. At STP, 1 mole of gas occupy 22.4 L of volume.

$$\therefore \text{Moles of helium in container, } \mu = \frac{44.8}{22.4} = 2 \text{ moles}$$

Now, helium is monoatomic, so, $C_V = \frac{3}{2}R$

Change in temperature,

$$\Delta T = T_2 - T_1 = 15^\circ\text{C} = 15\text{ K}$$

$\therefore$ Volume of gas remain constant

$$\therefore \Delta W = p\Delta V = 0 \Rightarrow \Delta Q = \Delta U + \Delta W$$

Amount of heat required, $\Delta Q = \Delta U = \mu C_V \Delta T$

$$= 2 \times \frac{3}{2} R \times 15 = 45 R$$

$$= 45 \times 8.31 = 374\text{ J}$$

29. A gaseous mixture contain 16 g of helium and 16 g of oxygen, then calculate the ratio of C_p/C_v of the mixture.

Sol. Moles of helium (μ_{He}) = $\frac{16}{4} = 4$

$$\text{Moles of oxygen } (\mu_{\text{O}_2}) = \frac{16}{32} = \frac{1}{2}$$

As helium is monoatomic, so degrees of freedom of helium, $f = 3$, so $C_{V_{He}} = \frac{f}{2} R = \frac{3}{2} R$

As oxygen is diatomic, so degrees of freedom of oxygen, $f = 5$, so

$$C_{V_{O_2}} = \frac{f}{2} R = \frac{5}{2} R$$

$$\therefore C_{V_{mixture}} = \frac{\mu_{He} C_{V_{He}} + \mu_{O_2} C_{V_{O_2}}}{\mu_{He} + \mu_{O_2}}$$

$$= \frac{4 \times \frac{3}{2} R + \frac{1}{2} \times \frac{5}{2} R}{4 + \frac{1}{2}} = \frac{29}{18} R$$

$$\gamma = \frac{C_p}{C_v} \quad [\text{of mixture}]$$

$$\gamma_{mixture} = 1 + \frac{R}{C_{V_{mixture}}} = 1 + \frac{R}{\frac{29}{18} R} = 1.62$$

[as $C_p - C_v = R$]

- 30.** Three moles of a diatomic gas is mixed with two moles of monoatomic gas. What will be the molecular specific heat of the mixture at constant volume? [given, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$]

Sol. For a monoatomic gas, i.e. $\gamma = \frac{5}{3}$

$$C_{V_1} = \frac{R}{\gamma - 1} = \frac{R}{\frac{5}{3} - 1} = \frac{3}{2} R$$

For a diatomic gas, i.e. $\gamma = \frac{7}{5}$

$$C_{V_2} = \frac{R}{\gamma - 1} = \frac{5}{2} R$$

By conservation of energy,

$$C_{V_{mixture}} = \frac{\mu_1 C_{V_1} + \mu_2 C_{V_2}}{\mu_1 + \mu_2}$$

$$= \frac{2 \times \frac{3}{2} R + 3 \times \frac{5}{2} R}{2 + 3} = \frac{3R + 7.5 R}{5} = 2.1 R$$

- 31.** What will be the mean free path of nitrogen gas at STP of given diameter of nitrogen molecule = $2 \text{ \AA}$?

Sol. Given, diameter of nitrogen molecule, $d = 2 \text{ \AA}$

$$= 2 \times 10^{-10} \text{ m}$$

At STP, one mole of gas (or 22.4 L) of gas have

$$N_A = 6.023 \times 10^{23} \text{ molecules}$$

$\therefore$ Number density of nitrogen molecules

$$n = \frac{N_A}{22.4 \text{ L}} = \frac{6.023 \times 10^{23}}{22.4 \times 10^{-3} \text{ m}^3} = 2.69 \times 10^{25} \text{ m}^{-3}$$

$\therefore$ Mean free path of nitrogen at STP condition,

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

$$\lambda = \frac{1}{1.414 \times 3.142 \times (2.69 \times 10^{25}) \times (2 \times 10^{-10})^2}$$

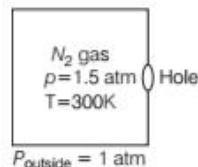
$$= 2.1 \times 10^{-7} \text{ m}$$

LONG ANSWER Type II Questions

- 32.** A box of 1.00 m^3 is filled with nitrogen at 1.50 atm at 300 K . The box has a hole of an area is 0.010 mm^2 . How much time is required for the pressure to reduce by 0.10 atm , if the pressure outside is 1 atm . [NCERT Exemplar]

Sol. Given, volume of the box, $V = 1.00 \text{ m}^3$

$$\text{Area, } a = 0.010 \text{ mm}^2 = 10^{-8} \text{ m}^2$$



Temperature outside = Temperature inside

Initial pressure inside the box = 1.50 atm .

Final pressure inside the box = 0.10 atm .

Assuming,

v_{ix} = Speed of nitrogen molecule inside the box along x-direction.

n_1 = Number of molecules per unit volume in a time interval of Δt , all the particles at a distance ($v_{ix} \Delta t$) will collide the hole and the wall, the particle colliding along the hole will escape out reducing the pressure in the box.

Let area of the wall is A , number of particles colliding in time, Δt

$$= \frac{1}{2} n_1 (v_{ix} \Delta t) A$$

$\frac{1}{2}$ is the factor because all the particles along x- direction are behaving randomly. Hence, half of these are colliding against the walls on either side.

Inside the box, $v_{ix}^2 + v_{iy}^2 + v_{iz}^2 = v_{rms}^2$

$$\Rightarrow v_{ix}^2 = \frac{v_{rms}^2}{3} \quad [\because v_{ix} = v_{iy} = v_{iz}]$$

If particles collide along hole, they move out. Similarly, outer particles colliding along hole will move in.

If a = area of hole

Then, net particle flow in time,

$$\Delta t = \frac{1}{2}(n_1 - n_2) \frac{k_B T}{m} \Delta t a \quad \left[\because v_{rms} = \sqrt{\frac{3k_B T}{m}} \right]$$

[Temperature inside and outside the box are equal]

Let n = number of density of nitrogen

$$n = \frac{\mu N_A}{V} = \frac{p N_A}{RT} \quad \left[\because \frac{\mu}{V} = \frac{p}{RT} \right]$$

Where, N_A = Avogadro's number

If after time Δt , pressure inside changes from p to p_1

$$\therefore n_1' = \frac{p_1' N_A}{RT}$$

Now, number of molecules gone out = $n_1 V - n_1' V$

$$= \frac{1}{2}(n_1 - n_2) \sqrt{\frac{k_B T}{m}} \Delta t a$$

$$\therefore \frac{p_1 N_A}{RT} V - \frac{p_1' N_A}{RT} V = \frac{1}{2}(p_1 - p_2) \frac{N_A}{RT} \sqrt{\frac{k_B T}{m}} \Delta t a$$

$$\Rightarrow \Delta t = 2 \left(\frac{p_1 - p_1'}{p_1 - p_2} \right) \frac{V}{a} \sqrt{\frac{m}{k_B T}}$$

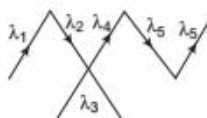
Putting the values from the data given,

$$\begin{aligned} \Delta t &= 2 \left(\frac{1.5 - 1.4}{1.5 - 1.0} \right) \frac{1 \times 100}{0.01 \times 10^{-6}} \sqrt{\frac{46.7 \times 10^{-27}}{1.38 \times 10^{-23} \times 300}} \\ &= \frac{2}{5} \times 3.358 \times 10^5 = \frac{6.717}{5} \times 10^5 = 1.343 \times 10^5 \text{ s} \end{aligned}$$

33. (i) Define mean free path.

(ii) Derive an expression for mean free path of a gas molecule.

Sol. (i) The mean free path of a gas molecule is defined as the average distance travelled by a molecule between two successive collisions.



According to figure, if a molecule covers free path $\lambda_1, \lambda_2, \lambda_3 \dots$ after successive collisions, then its mean free path is given by

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 \dots}{(\text{total number of collisions})}$$

(ii) Refer to text on page 476.

34. (i) What do you understand by specific heat capacity of water?

(ii) If one mole of ideal monoatomic gas ($\gamma = 5/3$) is mixed with one mole of diatomic gas ($\gamma = 7/5$). What is the value of γ for the mixtures?

(here, γ represents the ratio of specific heat at constant pressure to that at constant volume)

Sol. (i) Refer to text on pages 475 and 476.

(ii) For monoatomic gas, $C_V = \frac{3}{2} R$

For diatomic gas, $C_V' = \frac{5}{2} R$

Let, μ and μ' be moles of mono and diatomic gases

then, $C_V (\text{mixture}) = \frac{\mu C_V + \mu' C_V'}{\mu + \mu'}$

$$C_V = \frac{1 \times \frac{3}{2} R + 1 \times \frac{5}{2} R}{1 + 1} = 2 R$$

$$\gamma (\text{mixture}) = 1 + \frac{R}{C_{V(\text{mixture})}} = 1 + \frac{R}{2R} = 1.5$$

35. Estimate the mean free path and collision frequency of a nitrogen molecule in a cylinder containing nitrogen at 2.0 atm and temperature 17°C. Take the radius of a nitrogen molecule to be roughly 1.0 Å. Compare the collision time with the time, the molecule moves freely between two successive collisions

(molecular mass of $N_2 = 28.0 \text{ u}$).

[NCERT]

Sol. Let n be the number of molecules per unit volume of the gas. Now, $pV = NkT$, where N = number of molecules in volume V of the gas

$$\therefore n = \frac{N}{V} = \frac{p}{kT}$$

Here, $p = 2 \times 1.01 \times 10^5 \text{ N/m}^2$, $k = 1.38 \times 10^{-23} \text{ J/K}$

$$T = 273 + 17 = 290 \text{ K}$$

$$\begin{aligned} \therefore n &= \frac{2 \times 1.01 \times 10^5}{(1.38 \times 10^{-23}) \times (290)} \\ &= 5.05 \times 10^{25} \text{ molecules/m}^3 \end{aligned}$$

Mean free path,

$$\lambda = \frac{1}{4\pi\sqrt{2} r^2 n}$$

Here, $r = 1.0 \text{ Å} = 1.0 \times 10^{-10} \text{ m}$,

$$n = 5.05 \times 10^{25} \text{ molecules/m}^3$$

$$\therefore \lambda = \frac{1}{4\pi\sqrt{2} \times (1.0 \times 10^{-10})^2 \times 5.05 \times 10^{25}}$$

$$\lambda = 1.11 \times 10^{-7} \text{ m}$$

$$\text{Now, } v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 290}{28 \times 10^{-3}}} = 508.14 \text{ m/s}$$

$\therefore$ Collision frequency,

$$\begin{aligned} f &= \frac{v_{rms}}{\lambda} = \frac{508.14}{1.11 \times 10^{-7}} \\ &= 4.58 \times 10^9 \text{ collisions/s} \end{aligned}$$

ASSESS YOUR TOPICAL UNDERSTANDING

OBJECTIVE Type Questions

- A molecule moving along a straight line possess degree of freedom.
(a) one (b) two (c) three (d) four
- The value of γ for a diatomic molecule (vibrational mode) is
(a) $\frac{9}{7}$ (b) $\frac{7}{9}$ (c) $\frac{7}{5}$ (d) $\frac{5}{7}$
- During an adiabatic process, the pressure of a gas is found to be proportional to the cube of its temperature. The ratio of $\frac{C_p}{C_v}$ for the gas is
(a) $\frac{4}{3}$ (b) 2 (c) $\frac{5}{3}$ (d) $\frac{3}{2}$
- The value of C_v for solids is
(a) $3R$ (b) $2R$
(c) $4R$ (d) $3/2 R$
- As temperature tends to zero i.e., $T \rightarrow 0$
(a) specific heat of all substances approaches zero
(b) specific heat of all substances approaches infinity
(c) specific heat of all substances may be zero or infinity
(d) None of the above
- We took two separate gases with the same number densities for both. If the ratio of the diameters of their molecules is 4 : 1, then ratio of their mean free paths is
(a) 1 : 4 (b) 4 : 1 (c) 2 : 1 (d) 1 : 16

Answer

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (a) | 2. (a) | 3. (d) | 4. (a) | 5. (a) |
| 6. (d) | | | | |

VERY SHORT ANSWER Type Questions

- What is the value of degree of freedom for a diatomic rigid rotator (which do not show vibrational mode)?
- The speed of gas molecule is around the speed of sound, so why gas takes considerable time to diffuse?
- If the formula of mean free path is considered to be as $\bar{l} = \frac{1}{n\pi d^2}$, then find the condition for this particular formula.

- Which type of gas when the value of γ for a gas is $\frac{9}{7}$?

- Why diatomic molecule contributes only two rotational degrees of freedom?

SHORT ANSWER Type Questions

- What is the value of degree of freedom for a rotating fan?
- Find the value of degree of freedom for a cricket ball in projectile motion.
- Find the value of specific heat capacity for solids.
- Calculate the value of specific heat capacity for one mole of water in J/kg.

[Ans. 75 J/kg, for 1 mole]

- Does, $C_p - C_v = R$, is applicable for any type of gas whether it is mono, di and polyatomic? Discuss it in brief.

LONG ANSWER Type I Questions

- Describe law of equipartition of energy with the help of two examples.
- Estimate the value of γ for (i) monoatomic, (ii) diatomic and (iii) polyatomic gases.
- Calculate the mean free path and collision frequency of a nitrogen molecule in a cylinder containing nitrogen at 2 atm and temperature 17°C . Take the radius of a nitrogen molecule to be roughly $1.0 \text{ \AA}$. Compare the collision time with the time, the molecule moves freely between two successive collisions. Molecular mass of $\text{N}_2 = 28.0 \text{ u}$.

[Ans. 500 times]

- Explain the concept of absolute zero temperature on the basis of kinetic theory of gases.
- Three vessels of equal capacity have gases at the same temperature and pressure. The first vessel contains neon (monoatomic), the second contains chlorine (diatomic) and the third contains uranium hexafluoride (polyatomic). Do the vessels contain equal number of respective molecules same in three cases? If not, in which case, v_{rms} is largest?

LONG ANSWER Type II Questions

22. Estimate the average thermal energy of a helium atom at

(i) room temperature 27°C ,

(ii) at 10^5 K and

(iii) at 5000 K

[Ans. (i) $[6.2 \times 10^{-21}\text{ J}]$ (ii) $[2.1 \times 10^{-18}\text{ J}]$

(iii) $[10.5 \times 10^{-20}\text{ J}]$

23. Four moles of an ideal gas having $\gamma = 1.67$ are mixed with 2 moles of another ideal gas having $\gamma = 1.4$. Find the value of γ for resulting mixture of gases.

[Ans. 1.54]

24. Calculate the change in internal energy of 3 mole of neon gas when its temperature is raised by 20°C .

(Take, $R = 8.31\text{ J mol}^{-1}\text{K}^{-1}$)

[Ans. 7.48 J]

SUMMARY

- **Behaviour of gases** Gases at low pressure and high temperature much above that at which they liquify (or solidify), follow a relation.

$$pV = Nk_B T \text{ or } \frac{pV}{NT} = k_B = \text{constant}$$

For different gases, $\frac{p_1 V_1}{N_1 T_1} = \frac{p_2 V_2}{N_2 T_2} = \frac{p_3 V_3}{N_3 T_3} \dots = k_B = \text{constant}$ where, k_B = Boltzmann's constant and its value in SI unit is $1.38 \times 10^{-23}\text{ J/K}$.

- **Boyle's law** It states that for a given mass of a gas at constant temperature, the volume of that mass of gas is inversely proportional to its pressure.

i.e.

$$V \propto \frac{1}{p}$$

$\Rightarrow$

$$p_1 V_1 = p_2 V_2 = p_3 V_3 \dots = \text{constant}$$

- **Charles' law** It states that for a given mass of an ideal gas at constant pressure, volume (V) of a gas is directly proportional to its absolute temperature T

i.e.

$$V \propto T$$

$\Rightarrow$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} \dots = \text{constant}$$

- **Dalton's law of partial pressure** It states that the total pressure 'of a mixture of non-interacting ideal gases is the sum of partial pressures exerted by individual gases in the mixture.

i.e.

$$p = p_1 + p_2 + p_3 + \dots$$

Dalton's law,

$$p = p_1 + p_2 + p_3 + \dots$$

- **Graham's law of diffusion** It states that the rate of diffusion of a gas is inversely proportional to the square root of its density.

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

where, r = rate of diffusion and ρ = density of the gas.

- **Kinetic theory of ideal gas** Kinetic theory of gases is based on the molecular theory of matter. It correlates the macroscopic properties like pressure and temperature of gases to microscopic properties like speed and kinetic energy of gas molecules.

- **Root mean square speed** The square root of average of square velocities of gas molecules is known as root mean square speed. It is abbreviated as v_{rms}

$$\text{Root mean square speed, } v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$$

where, m = mass of one molecule

k_B = Boltzmann's constant and T = absolute temperature of the gas.

- **Mean square velocity** The average of square velocity of the gas is known as mean square velocity. It is abbreviated as

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

- **Most probable speed** The approximate speed with which maximum number of gas molecules move is known as most probable speed. The most probable speed is abbreviated as v_{mp} and given by

$$v_{mp} = \sqrt{\frac{2kT}{m}}$$

- **Average speed** The average speed of ideal gas molecules is given by

$$v_{av} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n} = \sqrt{\frac{8RT}{\pi m}}$$

- **Degree of freedom** The total number of coordinates axes of independent quantities required to describe completely the position and configuration of dynamical system (gaseous) is known as number of degrees of freedom of the system. It is represented by f and expressed as

$$f = 3N - K$$

where, N is the number of particles and K is number of coordinates of the particles.

- **Law of equipartition of energy** For a dynamic system in thermal equilibrium, the total energy is distributed equally amongst all the degree of freedom and the energy associated with each molecule per degree of freedom is

$$\frac{1}{2} k_B T.$$

- where, f = degree of freedom, N = number of particles and K = number of coordinates of the particles

- **Molar specific heat of gases** The molar specific heat of gases is the heat given per mole of the gas per unit rise in the temperature. Molar specific heat has two kind

- (i) Molar specific heat constant volume

$$C_V = \left(\frac{\Delta Q}{\Delta T} \right)_V \text{ or } C_V = \frac{f}{2} R$$

- (ii) Molar specific heat at constant pressure

Relation between C_p and C_V is given by

$$C_p = C_V + R \text{ or } C_p = \left(\frac{f}{2} + 1 \right) R = \frac{1}{n} \left(\frac{\Delta A}{\Delta T} \right)_p$$

- **Mean free path** It is the average distance between two successive collisions of a gas molecules and is given by

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

where, d = diameter of a molecule and n = number of molecules per unit volume.

It is also called the **number density** of the molecules.

CHAPTER PRACTICE

OBJECTIVE Type Questions

- Temperature remaining constant, the pressure of gas is decreased by 20%. The percentage change in volume
(a) increases by 20% (b) decreases by 20%
(c) increases by 25% (d) decreases by 25%
- The internal energy of an ideal gas is in the form of
(a) kinetic energy of molecules
(b) potential energy of molecules
(c) Both kinetic and potential energy of molecules
(d) gravitational potential energy of molecules
- According to the kinetic theory of gases, the temperature of a gas is a measure of average
(a) velocities of its molecules
(b) linear momenta of its molecules
(c) kinetic energies of its molecules
(d) angular momenta of its molecules
- An inflated rubber balloon contains one mole of an ideal gas, has a pressure p , volume V and temperature T . If the temperature rises to $1.1 T$, and the volume is increased to $1.05 V$, the final pressure will be [NCERT Exemplar]
(a) $1.1 p$ (b) p
(c) less than p (d) between p and $1.1 p$
- At what temperature the kinetic energy of gas molecule is half of the value at 27°C ?
(a) 13.5°C (b) 150°C (c) 75 K (d) -123°C
- The two gases with the ratio 3 : 2 of their masses in a container are at a temperature T . The ratio of the kinetic energies of the molecule of two gases is
(a) 3 : 2 (b) 9 : 4 (c) 1 : 1 (d) 4 : 9
- The ratio of the molar heat capacities of a diatomic gas at constant pressure to that at constant volume is
(a) $\frac{7}{2}$ (b) $\frac{3}{2}$
(c) $\frac{3}{5}$ (d) $\frac{7}{5}$

- The gases carbon monoxide (CO) and nitrogen (N_2) at the same temperature have kinetic energies E_1 and E_2 , respectively. Then,
(a) $E_1 = E_2$
(b) $E_1 > E_2$
(c) $E_1 < E_2$
(d) E_1 and E_2 cannot be compared
- The total energy for one mole of solid is
(a) $2 RT$ (b) $3 RT$ (c) $4 RT$ (d) $3/2 RT$

ASSERTION AND REASON

Direction (Q.Nos. 10-14) In the following questions, two statements are given- one labelled Assertion (A) and the other labelled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below

- Both Assertion and Reason are true and Reason is the correct explanation of Assertion.
 - Both Assertion and Reason are true but Reason is not the correct explanation of Assertion.
 - Assertion is true but Reason is false.
 - Assertion is false but Reason is true.
- Assertion** Molecules attract when they are little distance apart and repels when they come very close to each other.
Reason $F = -\frac{dU}{dr}$
 - Assertion** In gases, the molecules move faster and move long distances without colliding.
Reason In gases, the interatomic forces are negligible.
 - Assertion** The total translational kinetic energy of all the molecules of a given mass of an ideal gas is 1.5 times the product of its pressure and its volume.
Reason The molecules of a gas collide with each other and the velocities of the molecules change due to the collision.
 - Assertion** A gas can be liquified at any temperature by increase of pressure alone.
Reason On increasing pressure, the temperature of gas increases.

- 14. Assertion** Internal energy of an ideal gas does not depend upon volume of the gas.

Reason Internal energy of ideal gas depends on temperature of gas.

CASE BASED QUESTIONS

Direction (Q. Nos. 15-16) These questions are case study based questions. Attempt any 4 sub-parts from each question. Each question carries 1 mark.

15. Law of Equipartition of Energy

For a dynamic system in thermal equilibrium, the total energy is distributed equally amongst all the degree of freedom and the energy associated with each molecule per degree of freedom is $\frac{1}{2} k_B T$

where, $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is Boltzmann constant and T is absolute temperature of system on the kelvin scale. For a monoatomic gas in thermal equilibrium at temperature T , the average value of translational energy of the molecule is

$$\langle E_t \rangle = \left\langle \frac{1}{2} m v_x^2 \right\rangle + \left\langle \frac{1}{2} m v_y^2 \right\rangle + \left\langle \frac{1}{2} m v_z^2 \right\rangle$$

Translational energy of the molecules,

$$\langle E_t \rangle = \frac{3}{2} k_B T$$

- (i) Law of equipartition of energy is used to
 - (a) predict the specific heats of gases
 - (b) predict the specific heats of solids
 - (c) Both (a) and (b)
 - (d) Neither (a) nor (b)
- (ii) Diatomic molecule (rigid rotator) has
 - (a) 3 translational degrees of freedom
 - (b) 2 rotational degrees of freedom
 - (c) Both (a) and (b)
 - (d) All of the above
- (iii) Choose the correct option.
 - (a) Each translational mode contributes $\frac{1}{2} k_B T$ average energy.
 - (b) Each rotational mode contributes $\frac{1}{2} k_B T$ average energy.
 - (c) Vibrational mode contributes $k_B T$ average energy.
 - (d) All of the above

- (iv) Molecules of CO at moderate temperature have energy

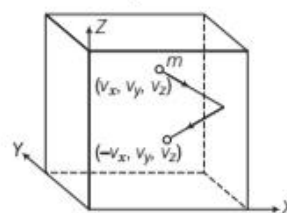
- (a) $\frac{7}{2} k_B T$
- (b) $\frac{5}{2} k_B T$
- (c) $\frac{3}{2} k_B T$
- (d) $\frac{1}{2} k_B T$

- (v) The mean kinetic energy of one mole of gas per degree of freedom (on the basis of kinetic theory of gases) is

- (a) $\frac{1}{2} k T$
- (b) $\frac{3}{2} k T$
- (c) $\frac{3}{2} R T$
- (d) $\frac{1}{2} R T$

16. Collision

A molecule of gas collides with the wall of a container elastically.



As collision is elastic only the x-component of the velocity changes after collision. It become reversed y and z-components of velocity do not change.

- (i) Momentum imparted to the wall due to collision of the molecule is
 - (a) $2m v_y$
 - (b) $2m v_x$
 - (c) $2m v_z$
 - (d) $m v_x$
- (ii) The total momentum imparted to the wall in time Δt on the area A of the wall due to molecules of velocity v_x is
 - (a) $n m v_x^2 A \Delta t$
 - (b) $n m v_x A \Delta t$
 - (c) $\frac{1}{2} n m v_x^2 A \Delta t$
 - (d) $\frac{1}{2} n m v_x A \Delta t$
- (iii) The expression of pressure due to the collision of molecules of velocity v_x is
 - (a) $n m v^2$
 - (b) $n m v_x^2$
 - (c) $n m v_x$
 - (d) $\frac{1}{2} n m v_x^2$
- (iv) The expression of total pressure to the group of molecules having velocities along the X-axis is
 - (a) $n m v_x^2$
 - (b) $n m \bar{v}_x^2$
 - (c) $n m v_x^2$
 - (d) None of these

(v) The general expression of pressure due to a gas is

- (a) $\frac{1}{2} nm \bar{v}^2$ (b) $\frac{1}{3} nm \bar{v}^2$
 (c) $nm \bar{v}$ (d) None of these
 where, $\bar{v}^2$ is mean of the square speed of a molecule.

Answers

- | | | | | |
|-------------|----------|-----------|----------|---------|
| 1. (c) | 2. (a) | 3. (c) | 4. (d) | 5. (d) |
| 6. (c) | 7. (d) | 8. (a) | 9. (b) | 10. (a) |
| 11. (a) | 12. (b) | 13. (d) | 14. (b) | |
| 15. (i) (c) | (ii) (c) | (iii) (d) | (iv) (a) | (v) (d) |
| 16. (i) (b) | (ii) (a) | (iii) (b) | (iv) (b) | (v) (b) |

VERY SHORT ANSWER Type Questions

17. Can an ideal gas be really obtained in practice?
18. Write the rms speed of molecules of a gas in terms of its pressure.
19. How rms speed of a gas vary with temperature?
20. Mention two conditions under which the real gases obey the ideal gas equation.
21. Smell of a scent spreads in whole room when few drops of it are poured on the table. Which phenomenon is responsible for it?
22. Name the factors on which degree of freedom of a gas depends.
23. What is the value of γ to monoatomic gas?
[Ans. 1.67]

SHORT ANSWER Type Questions

24. Draw p - V curves showing deviations from ideal behaviour for a given mass of a gas for two different temperatures.
25. What is Brownian motion?
26. Why does specific heat of gases increases with their atomicity?
27. For an ideal gas, show that, $C_p - C_v = \frac{R}{J}$.
28. What do you understand by degree of freedom?
29. What is the rms speed of hydrogen gas molecules at STP. Given, density is 0.09 kg m^{-3} .
[Ans. $1.8 \times 10^3 \text{ ms}^{-1}$]

30. Why temperature less than 0 K is not possible?

LONG ANSWER Type I Questions

31. Calculate the temperature at which the rms speed of CO_2 gas molecule will be 1 kms^{-1} .
Given that molecular mass of $\text{CO}_2 = 44 \text{ u}$
[Ans. $1.8 \times 10^3 \text{ K}$]
32. What is the kinetic energy of translation of one molecule of a gas at 300 K? Gas is having three degree of freedom. $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$.
[Ans. $6.21 \times 10^{-21} \text{ J}$]
33. State Charles' law, obtain it from kinetic theory of gases.
34. Establish ideal gas equation.
35. From kinetic theory of gases, can we obtain ideal gas equation? If yes, how?
36. State Dalton's law of partial pressure. Obtain it from kinetic theory of gases.
37. One mole of a monoatomic gas is mixed with three moles of a diatomic gas. What is the molar specific heat of the mixture at constant volume. ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)
[Ans. $2.25 R$]

LONG ANSWER Type II Questions

38. Calculate the mean free path of nitrogen gas at STP. Given the diameter of nitrogen molecule is $4 \text{ \AA}$.
[Ans. $5 \times 10^{-8} \text{ m}$]
39. What are the postulates of kinetic theory of gases? What will be expression for the pressure exerted by an ideal gas?
40. Using the law of equipartition of energy, show that for an ideal gas having f degree of freedoms is given by $\gamma = 1 + 2/f$.
41. What is Maxwell Boltzmann law with regard to speed distribution amongst molecules, state and explain?
42. What is the difference between atomic mass and atomic weight? Also, state what is the difference between NTP and STP.