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THERMODYNAMICS & STATISTICAL MECHANICS

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CHAPTER - 1

KINETIC THEORY OF GAS

INTRODUCTION

In agreement with the kinetic theory of matter, every substance whether a solid, liquid or gas, consists of a very large number of discrete particles called the molecules.

Molecules exist in Free State and possess all the characteristic properties of the parent substance. The molecules are in a state of continuous motion and their velocity increases with increase in temperature and molecules experience intermolecular forces of attraction.

In a solid, the molecules are closely packed so that the intermolecular forces are very large and they prevent the molecules from moving from one place to another. Due to this, the molecules can only vibrate about their mean positions. Therefore, a solid possesses a definite volume and shape. In liquids, the molecules are more separated than in solids and the intermolecular forces are relatively smaller. Therefore, the liquid molecules can move about inside the body of the liquid but cannot leave the liquid. For this reason, the liquids have a definite volume, but no definite shape. In the case of gases, the molecules are so far apart that the intermolecular forces are negligible. The molecules are completely free to move about and can occupy all the available space. Therefore, a gas can possess neither a definite shape nor a definite volume.

The kinetic theory of gases forms a part of the more general theory called the kinetic theory of matter.

Let us study in detail kinetic theory of gases in this chapter. On the basis of this theory, well known gas laws in physics and chemistry can be deduced.

Assumptions of Kinetic Theory of Gases:

The kinetic theory of gases is based on the following main assumptions, first stated by Clausius.

(1) A gas consists of a large number of extremely small molecules. At NTP, the number of molecules in $1\ cc$ of a gas is 2×10^{19}.
(2) The molecules of a gas are considered to be rigid, perfectly elastic, spherical, identical in all respects such as mass, volume, etc.
(3) The size of the individual gaseous molecules is infinitesimally small as compared to the volume of the gas.
(4) There is negligible force of attraction or repulsion between the gaseous molecules.
(5) The molecules are in a state of random motion, moving in all directions with all possible velocities. The velocity of molecules increases with temperature.
(6) The molecules in their random motion collide with one another. Such collisions are perfectly elastic i.e. there is no loss of kinetic energy during collisions.
(7) The time of impact is negligible in comparison with the time interval between successive collisions.
(8) Between two successive collisions, a molecule travels in a straight line with uniform velocity. The distance travelled by a molecule between the two successive collisions is called the free path of the molecule. The average distance travelled by a molecule between successive collisions is known as the mean free path.
(9) Though the molecules are constantly moving, the number of molecules per unit volume of the gas remain constant throughout the container.

A gas which satisfies all the above assumptions is called a perfect gas or ideal gas. On the basis of the kinetic theory, an expression for the pressure exerted by the gas can be derived, and is given by,

$$P = \frac{1}{3}\frac{Nmc^2}{V} = \frac{1}{3}\frac{M}{V}c^2 = \frac{1}{3}\rho c^2$$

where N is the total number of gas molecules in volume V, M is the total mass of the gas,ρ is the density of the gas, m is the mass of each gas molecule, and c is the root mean square(RMS) velocity of the gas molecules.

For 1 gram-molecule of a gas at$T°K$,

$$PV = \frac{1}{3}Nmc^2$$

From the perfect gas equation,

$$PV = RT$$

$\therefore \frac{1}{3}Nmc^2 = RT$

$\therefore \frac{2}{3}N\left(\frac{1}{2}mc^2\right) = RT$

$\therefore \frac{1}{2}mc^2 = \frac{3}{2}\frac{RT}{N_0} = \frac{3}{2}kT$ N_0 = Avogadro number

Where$k$ is called Boltzmann constant

$\therefore \frac{1}{2}mc^2 \propto T$

I.e. the average kinetic energy $(K.E.)$ of a gas molecule is directly proportional to theabsolute temperature of the gas.

From the above relation, we get

$$c^2 = \frac{3\,kT}{m} = \frac{3RT}{N\,m}$$

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

$= \frac{1}{3}\rho\frac{3kT}{m} = \frac{\rho kT}{m}$

And$c = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{N\,m}}$

$$Nm = M = Molecular\ wt.$$

$\because k = \frac{R}{N_0}$

$\therefore c \propto \sqrt{T}$

Thus, the R.M.S. velocity of the gas molecules is directly proportional to the square rootof the absolute temperature of the gas.

Kinetic Interpretation of Temperature:

The average kinetic energy of a molecule is defined as

$$\bar{E} = \frac{1}{2}mc^{-2}$$

Also the expression for the pressure exerted by the gas is given by

$$P = \frac{1}{3}\frac{Nmc^{-2}}{V}$$

$= \frac{1}{3}\frac{M}{V}c^{-2} = \frac{1}{3}\rho c^{-2}$

Where, N total number of molecules in volume V

M: mass of the gas

ρ: Density of the gas

m: mass of each molecule

$\bar{c}$: root mean square (RMS) velocity of the gas molecules

$$PV = \frac{2}{3}N\left(\frac{1}{2}mc^{-2}\right)$$

$$PV = \frac{2}{3}N\bar{E}$$

It is instructive to compare this equation with the ideal gas equation.

$$PV = \mu RT$$

Where $\mu = \frac{N}{N_0}$, is the number of kilo moles of gas, T is the absolute temperature and R isthe kilo molar gas constant. Its value is $8314\ J\ k\ mol^{-1}K^{-1} = 1.987\ kcal\ k\ mol^{-1}K^{-1}$.

Thus we have,

$$\frac{2}{3}\mu N_0\bar{E} = \mu RT$$

$$\bar{E} = \frac{3}{2}\frac{R}{N_0}T = \frac{3}{2}k_BT$$

The constant kg is called the Boltzmann constant. Its value is $1.38 \times 10^{23}\ J\ K^{-1}$.

This equation expresses the fact that the average kinetic energy per molecule of an ideal gas is proportional to the absolute temperature of the gas.

At $T = 0, \bar{E} = 0$

This implies that at absolute zero of temperature, the gas molecules will be devoid of all motion. This is the kinetic or molecular interpretation of absolute zero. In practice, $\bar{E}$ is thefinite indicating a deviation from ideal character. Average kinetic energy of a molecule is independent of pressure, volume or the type of molecules.

MEAN FREE PATH

The kinetic theory of gases assumes the molecules of a gas as point masses. These molecules move with large velocities of the order of $10^5\ m/s$. For example, the RMS speed of oxygen molecules is about $400\ m/s$. There is no force to restrain the motion of themolecules. Therefore, if a gas is contained in an open container due to large velocities ofmolecules, it should escape from it in no time. But which is not observed in practice. To overcome this discrepancy, Clausius suggested that every molecule possesses a finite, though very small diameter due to which it has a very small volume. Molecules without volume will never collide with each other. On the other hand, molecules with finite volume, as they move about, are bound to collide with each other. Due to the collision, there will be a change in the magnitude and direction of the velocity of the molecule. Thus between two successive collisions, the path traversed by a molecule will be a straight line path with a constant velocity. But at each collision the direction of the path changes. Hence the path of a single molecule consists of a series of short zig-zag paths as shown in Fig. 1.1.

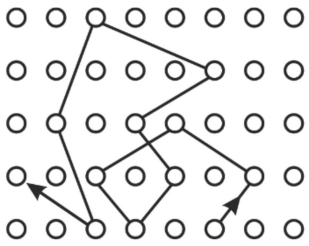


Fig. 1.1: Free path of a molecule

The distance travelled by a molecule between its two successive collisions is called the free path of the molecule. The free paths are not of the same length and hence the term mean free path is defined.

If $\lambda_1, \lambda_2, \lambda_3, \ldots \lambda_N$ are lengths of free paths during N successive collisions, the mean free path

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \cdots + \lambda_N}{N}$$

$$= \frac{Total\ distance\ travelled\ by\ a\ molecule\ in\ N\ collisions\ (S)}{Number\ of\ collisions\ (N)}$$

$$= \frac{S}{N}$$

Thus, the mean free path is defined as the average distance travelled by a molecule between successive collisions. The mean free path λ of a gas is of great importance instudying so called transport phenomena, such as viscosity, conduction of heat and diffusion.

Calculation of Mean Free Path:

In order to simplify the calculations, let us assume that only one molecule which is under consideration is moving while the remaining are at rest. Let n be the number ofmolecules per unit volume of the gas, σ be the diameter of each molecule and v be thevelocity of the moving molecule under consideration.

The moving molecule will collide with all the molecules whose centres lie within a distance σ from its centre (Fig. 1.2). In one second, the molecule will travel a distance $v$and hence it will collide with all the molecules whose centres lie in a cylinder of radius $\sigma$and length v.

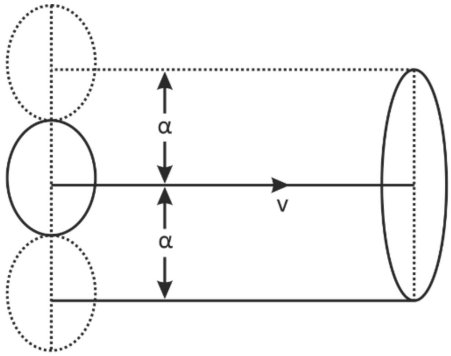


Fig. 1.2: A molecule moving in an assembly of 'static' molecules

The volume of the cylinder is $\pi\sigma^2 v$.

The number of molecules contained in this cylinder is $n\sigma^2 vn$. So the number ofcollisions made by the moving molecule in one second is $n\sigma^2 vn$. As the distance travelledin one second is v, the mean free path,

$$\lambda = \frac{\text{Distance travelled in one second}}{\text{Number of collisions in one second}}$$

$$\lambda = \frac{v}{\pi\sigma^2 vn}$$

$\therefore \lambda = \frac{1}{\pi\sigma^2 n}$ ..... (1.1)

If m is the mass of each molecule, then $mn = \rho$ is the density of the gas where n is thenumber of molecules per unit volume. From equation (1.1),

$$\lambda = \frac{m}{m\sigma^2 mn}$$

$= \frac{m}{\pi\sigma^2 mn}$ ..... (1.2)

Henceλ is inversely proportional to the square of the molecular diameter, andinversely proportional to the density of the gas.

The pressure P, of a gas is given by,

$$P = \frac{\rho kT}{m}$$

$\therefore \lambda = \frac{kT}{\pi\sigma^2 P}$ ..... (1.3)

Here the mean free path is directly proportional to the temperature and inversely proportional to the pressure of the gas.

All above expressions for λ are based on the assumption that a molecule collides withother stationary molecules, which is not the actual case. Maxwell considered the generalcase when all the molecules are moving with different velocities in different directions, and applied distribution law to get,

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

That is λ is inversely proportional to the square of the molecule diameter. Similarly, following relations can be obtained.

$$\lambda = \frac{m}{\sqrt{2}\pi\sigma^2\rho}$$

And $\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P}$

Problem: The diameter of He atom is $1\ A°$. One molecule of the gas occupies20 litres at $20\ K$. Calculate the mean free path of the molecules, the number of collisionsper unit distance and the collision frequency. Given $R = 8.4\ J\ mol^{-1}K^{-1}andN_A = 6 \times 10^{23}\ mol^{-1}$.

Solution: We know that,

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

$$\sigma = 1\ A° = 10^{-10}m$$

$$n = \frac{N_A}{V} = \frac{6 \times 10^{23}\ mol^{-1}}{20 \times 10^{-3}m^3\ mol^{-1}}$$

$= 3 \times 10^{25}m^{-3}$

Hence, $\lambda = \frac{0.707}{3.114\times(10^{-20}m^2)\times 3\times 10^{25}m^{-3}}$

$= 7.5 \times 10^{-7}\ m$

The number of collisions per unit distance is the inverse of the mean free path.

$\therefore N_S = \frac{1}{\lambda} = \frac{1}{7.5 \times 10^{-7}\ m}$

$= 1.33 \times 10^6 m^{-1}$

The average speed of a molecule obeying Maxwell's distribution is given by

$$\bar{c} = \left(2.55\frac{RT}{M}\right)^{\frac{1}{2}}$$

$= \frac{2.55 \times 8.4\ mol^{-1}K^{-1} \times 20\ K}{4 \times 10^{-3}\ kg\ mol^{-1}}$

$= 3.3 \times 10^2\ ms^{-1}$

Collision frequency is, $f = \frac{\bar{c}}{\lambda} = \frac{3.3\times 10^2\ ms^{-1}}{7.5\times 10^{-7}\ m}$

$$f = 4.4 \times 10^8 s^{-1}$$

Problem: The mean free path of the molecules of a gas at a pressure P and temperature T is $2 \times 10^{-7}\ m$. Calculate the m.f.p. if the temperature is doubled or thepressure is doubled.

Solution: We know that,

$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$where$n = \frac{P}{k_B T}$

$$\lambda = \frac{1}{\sqrt{2}}\frac{1}{\pi\sigma^2}\frac{k_B T}{P}$$

(a) When the temperature is doubled, this expression implies that the m.f.p. will increase by a factor of two. That is,

$$\lambda_{(P,2T)} = 2\ \lambda_{(P,T)} = 4 \times 10^{-7}\ m$$

(b) When the pressure is doubled, the mean free path will decrease by a factor of two.

Thus

$$\lambda_{(2P,T)} = \frac{1}{2}\lambda_{(P,T)}$$

$= 1 \times 10^{-7}\ m$

MAXWELL'S VELOCITY DISTRIBUTION LAW

The molecules of a gas move with velocities. These velocities are not equal. A molecule can have any velocity from zero to infinity in any direction. In a steady state, the distribution of velocities can be determined. Maxwell derived the distribution of the velocities of the molecules by statistical methods. Maxwell's statistical method is based on probability concept. The probability of an event is defined as the ratio of the number of favourable cases for the event to the total number of possible

cases, which are all equally probable. By applying such a method to the case of a gas consisting of an assembly of a very large number of molecules having velocity lying between zero and infinity, Maxwell deduced the following expression for the number of molecules dn possessing velocitiesbetween c and $c + dc$: (Proof given in Chapter-2 of Statistical Mechanics)

$dn = 4\,\pi n a^3 e^{-bc^2} c^2 dc$ …….. (1.4)

Where n is the number of molecules per unit volume, and a and b are constants which are related by

$$a = \sqrt{\frac{b}{\pi}}$$

With $b = \frac{m}{2\,kT}$

Equation (1.4) is known as Maxwell's law of distribution of velocities. This relation gives not the velocity of any individual molecule, but the probability that its velocity lies between c and $c + dc$ as:

$$4\pi a^3 e^{-bc^2} c^2 dc$$

Thus the distribution law gives a knowledge of the gas only in a statistical sense.

Graphical Representation and Most Probable Velocity:

According to Maxwell's velocity distribution law, the number of molecules dnpossessing velocities between c and $c + dc$ is given by,

$$dn = 4\pi n a^3 e^{-bc^2} c^2 dc$$

where, $a = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi\, kT}}$, a and b are constants.

Substituting the value of $b = \frac{m}{2kT}$ in the expression for dn we get

$dn = 4\pi\, n a^3 e^{-\frac{mc^2}{2\,kT}} c^2 dc$ ….. (1.5)

But kinetic energy$= \frac{1}{2}mc^2$

$\therefore\, dn = 4\pi\, n a^3 e^{-\frac{E}{kT}} c^2 dc$ …… (1.6)

Fig. 1.3 shows the graph of $\frac{dn}{dc}$versus c.

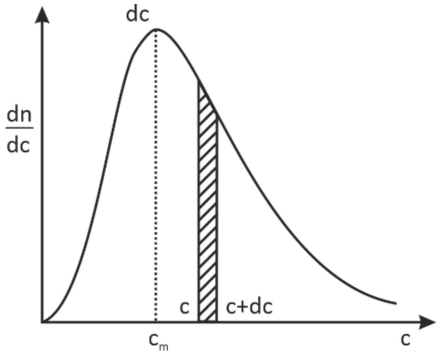


Fig. 1.3 : Maxwell's law of distribution of velocities

At a particular temperature T, the probability P, that a molecule having velocitybetween $c$and $c + dc$is given by,

$$P = \frac{dn}{dc} = 4\pi\, a^3 e^{-\frac{E}{kT}} c^2 dc$$

$P$is zero when $c = 0$ and $c = \infty$. Therefore, at a particular temperature, there must be somevelocity $c_m$between 0 and, for which the probability is maximum. This c_m is called themost probable velocity, and most of the molecules will have a velocity lying in theneighbourhood of c_m. For this velocity, dn, the number of molecules having velocitybetween c and $c + dc$, must be maximum.

$\therefore \frac{d}{dc}(dn) = 0$

From equation (1.5) we get

$$4\pi\, n a^3 \left\{ e^{\frac{-mc^2}{2\,kT}} \left(-\frac{\dot{m}c}{kT} c^2 + 2c \right) \right\}_{c=c_m} dc = 0$$

$\therefore 2 - \frac{mc_m^2}{kT} = 0$

$\therefore c_m = \sqrt{\frac{2\,kT}{m}}$

The expression gives the most probable velocity.

Average velocity $(\bar{c})$ and root mean square (RMS) velocity (c):

Average velocity and RMS velocity are given in integral form as follows:

(1) $\bar{c} = \frac{1}{n}\int_0^\infty c\, dn$

and (2) $\bar{c}^2 = \frac{1}{n}\int_0^\infty c^2\, dn$

The above integrals are particular cases of the integral

$$\frac{1}{n}\int_0^\infty c^r dn$$

Where r can take all integral values including zero. Integrals of this type appear in thestudy of various average properties depending on molecular velocities.

Substituting the value of dn from equation (1.57, we get,

$$\frac{1}{n}\int_0^\infty c^r dn = \frac{4\pi n a^3}{n}\int_0^\infty c^{r+2} e^{\frac{-mc^2}{kT}} \cdot dc$$

Putting, $\frac{m}{2kT} = b$ and $r + 2 = s$, we get,

$$\frac{1}{n}\int_0^\infty c^r dn = 4\pi a^3 \int_0^\infty c^5 e^{-bc^2} \cdot dc$$

If we take $r = 1$, then $s = 3$, or for odd values of s, we have

$$\frac{1}{n}\int_0^\infty c\, dn = 4\pi a^3 \int_0^\infty c^s e^{-bc^2} \cdot dc$$

$\therefore \bar{c} = 4\pi a^3 c^3 e^{-bc^2} \cdot dc$

Integrating by parts and for odd values of$s$ we get

$$\bar{c} = 4\pi a^3 \cdot \frac{1}{2b^2}$$

$\bar{c} = 4\pi a^3 \cdot \frac{1}{2\left(\frac{m}{2kT}\right)^2}$ $\qquad \left(\because b = \frac{m}{2kT}\right)$

$= \frac{8\pi a^3 k^2 T^2}{m^2}$

Again putting $a = \sqrt{\frac{m}{2\pi kT}}$, we have

$$\bar{c} = 8\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \frac{k^2 T^2}{m^2}$$

$\therefore \bar{c} = \sqrt{\frac{8kT}{m\pi}}$ $\qquad$ ..... (1.8)

Similarly for $r = 2$, and $s = r + 2 = 4$, or for even values of$s$, we have

$$\frac{1}{n}\int_0^\infty c^2 dn = 4\pi a^3 \int_0^\infty c^4 e^{-mc^2/2kT} \cdot dc$$

Integrating by parts for even values of s and for

$$a = \sqrt{\frac{m}{2\pi kT}}$$

$$\bar{c}^2 = \frac{3kT}{m}$$

So that the RMS velocity is given by,

$$c = \sqrt{\bar{c}^2} = \sqrt{\frac{3kT}{m}}$$

Thus RMS velocity c is equal to the square root of the average square velocity.
Thus we have,

(1) RMS velocity, $c = \sqrt{\frac{3kT}{m}}$

(2) Average velocity, $\bar{c} = \sqrt{\frac{8kT}{\pi m}}$

(3) Most probable velocity, $c_m = \sqrt{\frac{2kT}{m}}$

The Relations between RMS, Average, and Most Probable Velocities:

The relation between c, $\bar{c}$ and c_m is given by

$$c_m = \sqrt{\frac{2kT}{m}} = \left(\frac{\sqrt{\pi}}{2}\right)\sqrt{\frac{8kT}{m\pi}}$$

$= \left(\frac{\sqrt{\pi}}{2}\right)\bar{c}$ ..... (1.10)

$c_m = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2}{3}}\sqrt{\frac{3kT}{m}} = \sqrt{\frac{2}{3}} \cdot \bar{c}$ ..... (1.11)

$$\left(\because b = \frac{m}{2kT}\right)$$

Combining equations (1.10) and (1.11), we get

$$\frac{c_m}{\sqrt{2}} = \frac{c}{\sqrt{3}} = \frac{\bar{c}}{\frac{2\sqrt{2}}{\pi}} = \sqrt{\frac{kT}{m}}$$

Thus, it follows that

$$c_m^2 : \bar{c}^2 : c^2 :: 1 : 1.27 : 1.5$$

The most probable velocity c_m is less than the average velocity $\bar{c}$, which itself isslightly less than the RMS velocity c.

SOLVED EXAMPLE

1. Find the ratio of the speed of sound in an ideal gas to the root mean square speed of its molecules.

(a) $\sqrt{\frac{\gamma\pi}{8}}$ (b) $\sqrt{\frac{\gamma}{2}}$

(c) $\sqrt{\frac{\gamma}{3}}$ (d) $\sqrt{\frac{\gamma}{16}}$

Solution:

Speed of sound, $C_S = \sqrt{\frac{\gamma P}{\rho}}$

$$or, C_S = \sqrt{\frac{\gamma n K_B T}{mn}}$$

$$or, C_S = \sqrt{\frac{\gamma K_B T}{m}}$$

Where,

Pressure → $P = nK_BT$

Density → $\rho = mn$

K_B → Boltzmann constant

T → Temperature

Now, root mean square speed

$$V_{r.m.s} = \sqrt{\frac{3K_BT}{m}}$$

$\therefore \frac{C_S}{V_{r.m.s}} = \sqrt{\frac{\gamma}{3}}$

So, correct option is (c).

2. A beam of particles is passed through a low-pressure gas. The mean free path of particles in the gas is $5 \times 10^{-4}\ m$. What is the fractional attenuation in the intensity of the beam in traversing a thickness 10^{-2} mm of the gas sample? (Take e=2.718)

(a) 0.5 (b) 0.63

(c) 0.75 (d) 0.98

Solution:

We know a very well-known equation called "Survival equation" given by

$$N = N_0 e^{-x/\lambda}$$

Survival equation gives the number of molecules N (out of N_0) having free paths greater than x that is molecules that survived over a path length x.

Here,

$$e^{-x/\lambda} = e^{-\frac{10^{-2}}{5\times10^{-1}}}$$

$= e^{-\frac{1}{50}} = e^{-0.02}$

The intensity N, on traversing the thickness x, is therefore given by

$$N = N_0 e^{-x/\lambda}$$

Where,

$$N_0 = initial\ density$$

$\therefore$ Fractional attenuation in intensity.

$$\frac{N}{N_0} = e^{-x/\lambda} = e^{-0.02}$$

$$or, \frac{N}{N_0} = \left(\frac{1}{e}\right)^{0.02}$$

$\therefore \frac{N}{N_0} = 0.98$

As $e = 2.718$

So, (d) is correct option.

3. An ideal gas expand adiabatically so that its volume is quadruped. How many times will be number of collisions per second of the molecules decreases? ($\gamma = 1.40$)

(a) 1.14 (b) 1.32

(c) 1.98 (d) 2.46

Solution:

Let $\bar{Z}$ be the number of collisions/second. So, the mean free path is given by

$$\lambda = \frac{\bar{v}}{\bar{Z}} = \frac{1}{\sqrt{2}\,\pi\sigma^2 n}$$

$\bar{v}$ →Average velocity of the molecule

$$\bar{Z} = \bar{v}\sqrt{2}\,\pi\sigma^2 n$$

$$or, \bar{Z} = \sqrt{\frac{8K_BT}{\pi m}}\sqrt{2}\,\pi\sigma^2 n$$

$$\therefore \bar{Z} \propto \sqrt{T}$$

Now, as the process is adiabatic.

$TV^{\gamma-1} = \frac{T}{\rho^{\gamma-1}} = constatnt, we\ have$

$$\frac{T_1}{T_2} = \left(\frac{\rho_1}{\rho_2}\right)^{\gamma-1} = 4^{\gamma-1}$$

Since, $\frac{\rho_1}{\rho_2} = \frac{4}{1}$

$\therefore \frac{\overline{Z_1}}{\overline{Z_2}} = \frac{\sqrt{T_1}}{\sqrt{T_2}} = 4^{\frac{1}{2}(\gamma-1)} = 4^{\frac{1}{5}} = 1.32$

So, no of collision/sec would decreases 1.32 times.

So, (b) is correct option.

4. A beam of molecules is often produced by letting gas escape into a vacuum through a very small hole in the side of the container confining the gas. The total intensity of the beam is defined as the number of molecules escaping from the hole per unit time. Find the change in total intensity of the beam if