

Postulates of Kinetic Theory

Suppose a container with volume *V* contains a very large number of identical molecules *N*, each of mass *m*. Then, the kinetic theory postulates the following :

(a) The molecules behave as point particles as compared to the size of the container and as compared to the average distance between the molecules. So, the volume of the molecules can be neglected as compared to the volume of the container and hence

the total volume occupied by the molecules is same as the volume of the container. (b) The molecules are in constant motion in all the possible directions in a random manner. Each molecule

collides occasionally with the walls of the container and with each other as well. These collisions are perfectly elastic.

So, the molecules possess kinetic energy which is translational in nature only as the molecules are point particles and hence they can not rotate and vibrate but translate only.

(c) There is no force of attraction among the gas molecules and between the gas molecules and walls of the container.

So, the molecules do not possess any potential energy.

- (d) The container walls are rigid and infinitely massive and do not move.
- (e) The molecules obey Newton's law of motion.
- (f) The average time of collision is much less than the averaged time between two successive collision.

Pressure Exerted by the Gas

Frow does pressure of the gas originate. During comsions, the morecules exert forces How does pressure of the gas originate ? During collisions, the molecules exert forces on the walls of the

Steps to calculate the pressure exerted by gas molecules on the walls of the container

- 1. Number of collisions that occur per unit time for a certain area *A* of the wall.
- 2. Total momentum associated with these collisions
- 3. Force needed to cause this momentum change.

Assuming that all molecules in the gas have the same magnitude of *x*- component of velocity, $|v_x|$, we have

For each collision the *x*-component of velocity changes from $-|v_x|$ to $|v_x|$

So, the change in the momentum is $\Delta p_r = m|v_r| - (-m|v_r|) = 2m|v_r|$ (1)

If a molecule is going to collide with a given wall of area *A* during a small time interval *dt*, then at the beginning of time *dt* if must be within a distance v_x/dt from the wall and it must be headed toward the wall.

So, total number of molecules that collide with area *A* during time interval $dt \equiv$ Number of molecules within the cylinder with base area *A* and length $|v_x|dt$ and leading towards the wall,

where volume of cylinder $= A|v_x| dt$

Assuming uniform distribution of molecules, number of molecules in this cylinder $= \frac{1}{|X|} (A|v_x|dt)$ $\frac{N}{\sigma}$ ^{$(A|v_x|dt)$} *V* $=\left(\frac{N}{V}\right)($

On the average, half of these molecules are moving towards the wall (that causes pressure) and half are moving away from it.

So, number of collision with *A* during
$$
dt = \frac{1}{2} \left(\frac{N}{V} \right) \left(A |v_x| dt \right)
$$
 ... (2)

Due to all molecules in the gas, the total momentum change during *dt* is

$$
dp_x = (\text{No. of collisions}) \times 2m|v_x|
$$

\n
$$
= \frac{1}{2} \left(\frac{N}{V} \right) (A|v_x|dt) \times 2m|v_x|
$$

\n
$$
= \frac{NAm}{V} v_x^2 dt \qquad \left[\frac{|v_x|^2}{V} = v_x^2 \right]
$$

\n
$$
\Rightarrow \frac{dp_x}{dt} = \frac{NAm v_x^2}{V}
$$
 (3)

at v
According to Newton's second law, this rate of change of momentum equals the force exerted by the wall area *A* on the gas molecules. From Newton's III law, this is equal and opposite to the force exerted on the wall by the molecules.

So pressure *P*, the magnitude of the force exerted on the wall per unit area, is

$$
P = \frac{F}{A} = \frac{dp_x}{Adt} = \left(\frac{N}{V}\right)mv_x^2 \qquad \qquad \dots (4)
$$

Hence, pressure exerted by the gas depends on the number of molecules per unit volume (*N*/*V*), the mass m per molecule, and the speed of the molecules.

Note: $|v_x|$ is really not the same for all the molecules. But we could have sorted the molecules into groups

having the same $\vert v_x\vert$ with each group, where net effect of the molecules is $\left(v_x^2\right)_{i}$ v_x^2 _{$_{avg}$}.

Also, speed ν of 'a' molecules is

 $2^2 - 3^2 + 3^2 + 3^2$ $v^2 = v_x^2 + v_y^2 + v_z^2$

$$
\left(v^2\right)_{avg} = \left(v_x^2\right)_{avg} + \left(v_y^2\right)_{avg} + \left(v_z^2\right)_{avg}
$$
 ... (5)

Since there is no real difference in our model between $x-$, $y-$ and $z-$ direction, we have

$$
\langle v_x^2 \rangle_{avg} = (\nu_y^2)_{avg} = (\nu_z^2)_{avg}
$$

\n
$$
\therefore \quad \langle v^2 \rangle_{avg} = 3 \langle v_x^2 \rangle_{avg}
$$

\n
$$
\Rightarrow \quad (\nu_x^2)_{avg} = \frac{1}{3} (\nu^2)_{avg}
$$
 \n...(6)

Using equation (4), we have

$$
P = \frac{1}{3} \frac{N}{V} m (v^2)_{avg}
$$

\n
$$
\Rightarrow \boxed{PV = \frac{1}{3} N m (v^2)_{avg}} \quad [\because (v^2)_{avg} = (\overline{v}^2) = \langle v^2 \rangle \quad \dots (7)
$$

If ρ be the mass density of the gas, then

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

So,
$$
P = \frac{1}{3} \rho (v^2)_{avg}
$$

Problem : One mole of a gas is contained in a cube of side 0.2 m. If these molecules, each of mass 5×10^{-26} kg, move with the translational speed 483 ms⁻¹, calculate the pressure exerted by the gas on the sides of the cube.

(a) 2.9×10^5 N/m² (b) 2.9×10^6 N/m² (c) 5.8×10^5 N/m² (d) 5.8×10^6 N/m²

Soln. Given : $V = (0.2)^3 m^3$, $m = 5 \times 10^{-26} kg$, $n = 1$ mole, $v = 483$ m/s

The pressure is given by

$$
P = \frac{1}{3} \frac{mN}{V} (v^2)_{\text{avg}}
$$

= $\frac{1}{3} \times \frac{5 \times 10^{-26} \times 6.023 \times 10^{23}}{(0.2)^3} \times (483)^3$

 $= 1.65$ kPa.

Correct option is (a)

Problem : The r.m.s. speed of nitrogen at STP, if the density of nitrogen is 1.25 kg-m**–**³ at these conditions is (a) 490 km/s (b) 490 mm/s (c) 490 m/s (d) 490 m/s

Soln. Given: $P = 1 \text{ atm}, \rho = 1.25 \text{ kg} \cdot \text{m}^{-3}$

The pressure of the gas is

$$
P = \frac{1}{3} \rho(v^2)_{\text{avg}}, \text{ where } v_{\text{r.m.s}} = \sqrt{(v^2)_{\text{avg}}}
$$

$$
\therefore \qquad P = \frac{1}{3} \rho(v_{\text{r.m.s}})^2 \Rightarrow v_{\text{r.m.s}} = \sqrt{\frac{3P}{\rho}}
$$

$$
\Rightarrow \qquad v_{\text{r.m.s}} = \sqrt{\frac{3 \times 1 \times 1.01 \times 10^5}{1.25}} \approx 492 \text{ m/s}.
$$

Correct option is (c)

(a) Relation between pressure, volume and translational kinetic energy :

Now the average translational Kinetic energy (K.E) of a single molecule $=\frac{1}{2}m(v^2)$ $=\frac{1}{2}m(v^2)_{avg}$.

So the average total random kinetic energy *E* of translational motion of all the molecules is

$$
E = \frac{N}{2}m(v^2)_{avg}
$$
 ... (8)

Equations (7) and (8) \Rightarrow $\begin{array}{|l} P_V = \frac{2}{3} \end{array}$ 3 \Rightarrow $\mid PV = \frac{2}{3}E \mid$... (9)

- **Problem :** Calculate the number of molecules in 1 litre of an ideal gas at 1.5 atm pressure. The mean K.E. of a molecule is 4×10^{-11} J.
	- (a) 5.68×10^{12} (b) 5.68×10^{13} (c) 5.68×10^{4} (d) 5.68×10^{14}
- **Soln.** Given : $V = 1L$, $P = 1.5$ atm, $E_{1 \text{ molecule}} = 4 \times 10^{-11}$ J

The total average thermal energy is

$$
E_{N \text{ molecules}} = \frac{3}{2} PV
$$

= $\frac{3}{2} \times (1.5 \times 1.01 \times 10^5 \text{ Nm}^{-2}) \times (1 \times 10^{-3} m^3)$
= 227.25 J

Therefore, required number of molecules, $N = \frac{227.25}{4 \times 10^{-11}} = 5.68 \times 10^{12}$. $N = \frac{224 \cdot 125}{4 \times 10^{-11}} = 5.68 \times 1$ \times

Correct option is (a)

(b) Average thermal translational kinetic energy : Comparing with ideal gas equation

$$
PV=nRT,
$$

where *n* is the number of moles of the gas and *T* is the absolute temperature, we have

$$
E = \frac{3}{2}nRT
$$
 ... (10)

This is average thermal translational kinetic energy of '*n*' moles of an ideal gas which clearly shows that translational kinetic energy depends only on the temperature of the gas.

Now, average translational kinetic energy of '*a*' single molecule is given by

$$
=\frac{E}{N}=\frac{3 nRT}{2 N}, \text{ where } n=nN_A \tag{11}
$$

So,
$$
\frac{E}{N} = \frac{3}{2} \left(\frac{R}{N_A} \right) T
$$
 ... (12)

The ratio *A R* $\frac{R}{N_A}$ occurs frequently in molecular theory. It is called Boltzmann's constant k_B .

So, average kinetic translational energy of a molecule = 3 $\frac{3}{2}k_BT$

Problem : What is the average translational kinetic energy of a molecule in 1 mole of a gas at 27^oC ?

(a) 6.21×10^{-21} J (b) 6.21×10^{-22} J (c) 6.21×10^{-23} J (d) 6.21×10^{-20} J **Soln.** Given : $T = 27 \degree C = 300 \text{ K}$

Average translational kinetic energy per molecule $=\frac{3}{3}$ $=\frac{3}{2}k_B T = \frac{3}{2} \times 1.381 \times 10^{-23} \times 300$ 2 $=\frac{3}{2} \times 1.381 \times 10^{-23} \times 300 = 6.21 \times 10^{-21}$ J

Correct option is (a)

 ${\bf Problem:}$ The average translational kinetic energy of $\rm O_{2}$ (molar mass 32) molecules at a particular temperature is 0.048 eV. The translational kinetic energy of N_2 (molar mass 28) molecules in eV at the same temperature is

(a) 0.0015 (b) 0.003 (c) 0.048 (d) 0.768 **Soln.** Average translational kinetic energy of an ideal gas molecule is $3/2$ k_BT which depends on temperature only. Therefore, if temperature is same, translational kinetic energy of O_2 and N_2 both will be equal. **Correct option is (c)**

(c) Molecular Speeds : Root-mean-square speed (*v rms* **)**

The average translational kinetic energy of a molecule is equals to 3 $\frac{3}{2}k_BT$.

Also , from the basic definition of kinetic energy, the average translational kinetic energy of a molecule must

also be equals to
$$
\frac{1}{2}m(v^2)_{avg.}
$$
 So,

$$
\frac{1}{2}m(v^2)_{avg.} = \frac{3}{2}k_BT
$$
 ENDEAVOUR ... (13)

 $\binom{2}{2}$ where square-root of (v^2) v^2 $\bigg|_{avg}$ = Root-mean square speed (or r.m.s. speed) v_{rms}

$$
\therefore \quad \boxed{v_{\rm rms} = \sqrt{\left(v^2\right)_{\rm avg} = \sqrt{\frac{3k_B T}{m}}} = \sqrt{\frac{3RT}{M}} \qquad \left[\because k_B = \frac{R}{N_A}\right] \qquad \qquad \dots (14)
$$

where *M* is the molar mass of the gas and is equal to mN_A .

Problem : What is the root-mean-square speed of a molecule of hydrogen gas at room temperature? (a) 1.93 m/s (b) 19.3 km/s (c) 19.3 m/s (d) 1.93 km/s

Soln. Molar mass of hydrogen gas, $M = 2 \times 10^{-3}$ kg

$$
\therefore v_{\text{r.m.s.}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 300}{2 \times 10^{-3}}} \qquad [\because T = 300 \text{ K (room temperature)}]
$$

 $= 1.93$ km/sec **Correct option is (d)**

$$
\left[\begin{matrix}\hline\\[-1.5mm]\hline\\[-1.
$$

Problem : According to the kinetic theory of gases, the root-mean-square speed of gas molecules in a monoatomic ideal gas at a temperature *T* is

(a)
$$
\sqrt{\langle v \rangle^2} = \sqrt{\frac{k_B T}{m}}
$$
 (b) $\sqrt{\langle v \rangle^2} = \sqrt{\frac{k_B T}{2m}}$ (c) $\sqrt{\langle v \rangle^2} = \sqrt{\frac{3k_B T}{m}}$ (d) $\sqrt{\langle v \rangle^2} = \sqrt{\frac{k_B T}{3m}}$ [H.C.U.-2012]

Soln. The root mean square speed is

$$
v_{\text{r.m.s}} = \sqrt{\langle v \rangle^2} = \sqrt{\frac{3k_B T}{m}}
$$

Correct option is (c)

- **Problem :** Assuming that the hydrogen molecules have a root-mean-square speed of 1,270 m/s at 300 K, calculate the rms at 600 K.
	- (a) 179.6 m/s (b) 1796 m/s (c) 2796 m/s (d) 279.6 m/s

Soln. Given: $(v_{r,m,s})_1 = 1270 \text{ m/s}$, $T_1 = 300 \text{ K}$ and $(v_{r,m,s})_2 = ?$, $T_2 = 600 \text{ K}$

Since,
$$
(v_{\text{r.m.s.}}) = \sqrt{\frac{3k_B T}{m}} \Rightarrow \frac{(v_{\text{r.m.s.}})_1}{(v_{\text{r.m.s.}})_2} = \sqrt{\frac{T_1}{T_2}}
$$

\n $\Rightarrow (v_{\text{r.m.s.}})_2 = \sqrt{\frac{T_2}{T_1}} (v_{\text{r.m.s.}})_1 = \sqrt{2} \times 1270 = 1796 \text{ m/s.}$

Correct option is (b)

Problem : At room temperature, the rms speed of the molecules of a certain diatomic gas is found to be 1930 m/s. The gas is

(a) H₂ (b) F₂ (c) O₂ (d) Cl₂
\n**Soln.** We have,
$$
v_{\text{rms}} = \sqrt{\frac{3RT}{M}}
$$
 and room temperature $T \approx 300 K$
\n
$$
\therefore \qquad 1930 = \sqrt{\frac{3 \times 8.31 \times 10^3 \times 300 \text{ A}}{M}}
$$
\n
$$
\therefore \qquad M = 2.0 \text{ g/mol and hence, the gas is H.}
$$

$$
\therefore \qquad M = 2.0 \text{ g/mol and hence, the gas is H2.
$$

Correct option is (a)

Problem : Estimate the temperature at which the root-mean-square velocity of nitrogen molecule in earth's atmosphere equals the escape velocity from earth's gravitational field. Take the molar mass of nitrogen molecule = 28 gm / mol and radius of earth = 6*,*400 km.

(a) 1.4×10^6 K (b) 1.4×10^7 K (c) 1.4×10^5 K K (d) 1.4×10^4 K

Soln. Given: $M = 28$ g/mol, $R_e = 6400$ km

We have, $v_{r.m.s} = v_{es}$

$$
\Rightarrow \sqrt{\frac{3RT}{M}} = \sqrt{2gR_e}
$$

$$
\Rightarrow T = \frac{2gR_e}{3R}
$$

$$
=\frac{2 \times 10 \times 6.4 \times 10^{6} \times 28 \times 10^{-3}}{3 \times 8.314}
$$

$$
\simeq 1.4 \times 10^5 K.
$$

Correct option is (c)

 $\frac{1}{5}$

Problem : Five gas molecules chosen at random are found to have speeds of 500, 600, 700, 800 and 900 m/s? What

is the rms speed and average speed?

(a)
$$
v_{\text{rms}} = 700 \text{ m/s}
$$
 and $v_{\text{av}} = 714 \text{ m/s}$
\n(b) $v_{\text{rms}} = 71.4 \text{ m/s}$ and $v_{\text{av}} = 70.4 \text{ m/s}$
\n(c) $v_{\text{rms}} = 714 \text{ m/s}$ and $v_{\text{av}} = 700 \text{ m/s}$
\n(d) $v_{\text{rms}} = 70.4 \text{ m/s}$ and $v_{\text{av}} = 71.4 \text{ m/s}$

Soln. Given:
$$
v_1 = 500
$$
 m/s, $v_2 = 600$ m/s, $v_3 = 700$ m/s, $v_4 = 800$ m/s, $v_5 = 900$ m/s

$$
v_{\text{avg.}} = \frac{\sum_{i=1}^{5} v_i}{5} = \frac{500 + 600 + 700 + 800 + 900}{5} = 700 \text{ m/s}
$$

and $v_{\text{r.m.s.}} = \left(\frac{\sum_{i=1}^{5} v_i^2}{5}\right)^{1/2} = \left(\frac{500^2 + 600^2 + 700^2 + 800^2 + 900^2}{5}\right)^{1/2} = 714.14 \text{ m/s}$

Correct option is (c)

Problem : One gram mole of oxygen at 27^oC and one atmospheric pressure is enclosed in a vessel.

- (a) Assuming the molecules to be moving with $v_{\rm rms}$, find the number of collisions per second which the molecules make with one sqaure metre area of the vessel wall.
- (b) The vessel is next thermally insulated and moved with a constant speed v_0 . It is then suddenly stopped. The process results in a rise of the temperature of the gas by 1° C. Calculate the speed v_{0} .

 $\mathbf{I} = \mathbf{I}$

Soln. (a)
$$
v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 300}{32 \times 10^{-3}}} = 483.4 \text{ m/s}
$$

So, change in momentum per m² is $(2nmv_{rms})$.
Hence, the pressure is $P = 2nmv$. Let n molecules of oxygen strike the wall per second per m^2 and recoil with same speed.

Hence, the pressure is $P_0 = 2nmv_{\text{rms}}$

$$
\therefore \qquad n = \frac{P_0}{2m v_{\text{rms}}} = \frac{1.01 \times 10^5}{2 \left[\frac{32}{6.02 \times 10^{26}} \right] (483.4)} = 1.96 \times 10^{27} \text{ per sec}
$$

(b) For this, we have

$$
\frac{1}{2} (m_{\text{gas}}) v_0^2 = nC_V \Delta T
$$

$$
\therefore v_0 = \sqrt{\frac{2nC_V \Delta T}{m_{\text{gas}}}} = \sqrt{\frac{(2) (n) (\frac{5}{2} \times 8.31)(1)}{(6.02 \times 10^{26})(32)}} = 36 \text{ m/s}
$$

Problem : A cubical box of side 1 m contains helium gas (atomic weight 4 units) at a pressure of 100 N/m². During an observation time of 1 s, an atom travelling with the root mean square speed parallel to one of the edges of the cube, was found to make 500 hits with a particular wall, without any collision with other atoms. Take,

$$
R = \frac{25}{3}
$$
 J/mol-K and $k_B = 1.38 \times 10^{-23}$ J/K.

- (a) Evaluate the temperature of the gas.
- (b) Evaluate the average kinetic energy per atom.
- (c) Evaluate the total mass of helium gas in the box.
- **Soln.** Given : Volume of the box $= 1 \text{ m}^3$

Pressure of the gas = 100 N/m² Let T be the temperature of the gas. Then,

(a) Time between two consecutive collisions with one wall $=$ $\frac{1}{500}$ s 500 $=\frac{1}{500}$ s. This time should be equal to rms 2*l v* , where

l is the side of the cube.

(c) From $PV = nRT = \frac{m}{N}RT$ *M* , we have

We get mass of helium gas in the box, $m = \frac{PVM}{PR}$ *RT*

Substituting the values, we get

$$
m = \frac{(100)(1)(4)}{(25/3)(160)} = 0.3 \text{ g}
$$

Molecular Speeds Distribution

The molecules in a gas don't have the same speed rather the molecules posses a value of speed that lies from zero to infinity and hence the speeds are distributed among the molecules. So we will study a function $f(v)$ that will help us to know how a particular number of molecules possess a certain amount of speed. This function is called molecular speed distribution function.

If we observe *dN* molecules out of total *N* molecules having speed lies from *v* to $v + dv$, the corresponding fraction or the probability is given by

$$
\frac{dN}{N} = f(v) dv \qquad \qquad \dots (15)
$$

The Maxwell-Boltzmann Speed Distribution

The function $f(v)$ describing the actual distribution of molecular speeds is called the *Maxwell-Boltzmann speed distribution function*.

Deriving from the statistical physics, it is, in 3-dimensions, equals to

$$
f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}} , 0 \le v < \infty \quad ...(16)
$$

where *m* is the mass of a molecule of the gas

v is the speed of the molecules which is different for different group of molecules.

 T is the absolute temperature.

In terms of number of moles, the distribution function is

$$
f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}}
$$

The graph representing Maxwell-Boltzmann distribution function is

- (a) The graph is not symmetrical.
- (a) The graph is not symmetheal.
(b) At each temperature, the height of the curve for any value *v* is proportional to the number of molecules with speeds near *v*.
- (c) The area A_1 represents the fraction or the probability that some molecules (say N_1) have speed lies between v_1 and v_2 . Mathematically,

$$
A_{\rm I} = \int_{v_1}^{v_2} f(v) dv = \int \frac{dN}{N} = \frac{N_1}{N},
$$

where *N* is the total number of molecules.

(d) The total area under the curve is given by

$$
A = \int_{0}^{\infty} f(v) dv = 4\pi \left(\frac{m}{2\pi k_{B}T} \right)^{3/2} \int_{0}^{\infty} v^{2} e^{-mv^{2}/2k_{B}T} dv
$$

Using $\int_{0}^{\infty} x^{n} e^{-ax^{2}} dx = \frac{\boxed{(n+1/2)}}{2a^{\frac{n+1}{2}}}$, we have

$$
A = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{\sqrt{3/2}}{2\left(\frac{m}{2k_B T}\right)^{3/2}} = 1
$$

So the total area under the curve is unity. This is because the sum of the total probability is one.

- (e) There are very few number of molecules having very slow speed and very large speed as well.
- (f) There is a speed corresponds to which the function $f(v)$ is maximum. It means the maximum number of molecules possesses speed near this particular value of speed. We call this speed as the most probable speed (v_p) .
- **Problem :** A quantity of gas containing *N* molecules has a speed distribution function $f(v)$. How many molecules have speeds between and v_1 and v_2 ?

(a)
$$
\int_{0}^{v_2} f(v) dv - \int_{0}^{v_1} f(v) dv
$$

\n(b) $N \begin{bmatrix} v_2 \\ \int_{0}^{v_2} f(v) dv - \int_{0}^{v_1} f(v) dv \end{bmatrix}$
\n(c) $\int_{0}^{v_1} f(v) dv - \int_{0}^{v_2} f(v) dv$
\n(d) $N \begin{bmatrix} v_1 \\ \int_{0}^{v_1} f(v) dv - \int_{0}^{v_2} f(v) dv \end{bmatrix}$
\n**Soln.** Required number $= \int_{v_1}^{v_2} N f(v) dv = N \begin{bmatrix} \int_{0}^{v_2} f(v) dv - \int_{0}^{v_1} f(v) dv \end{bmatrix}$

Correct option is (b)

Various Speeds Possess by the Molecules

- (a) The average speed $(v_{avg}/\langle v \rangle/\overline{v})$:
- **(i) Definition :** It is the average speed possesses by the molecules of the gas.
- **(ii) Calculation :** It is given by

$$
v_{avg} = \int_0^\infty v f(v) dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv
$$

Using $\int_0^\infty x^n e^{-ax^2} dx = \frac{\Gamma\left(\frac{n+1}{2}\right)}{\frac{n+1}{2}}$, we have

Using
$$
J_0
$$
 $x e^{-\frac{n+1}{2a^2}}$, we have $2a^{-\frac{n+1}{2}}$

$$
v_{avg} = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{\Gamma 2}{2\left(\frac{m}{2k_B T}\right)^2} = \frac{4\pi}{\pi^{3/2}} \left(\frac{m}{2k_B T}\right)^{-\frac{1}{2}} \frac{1}{2} = \sqrt{\frac{8k_B T}{\pi m}} \qquad \dots (18)
$$

$$
\Rightarrow \boxed{v_{avg} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \quad \dots (19)}
$$

- **(b) Most probable speed** (v_{mp}) :
- **(i) Definition :** The maximum number of molecules possess speeds near a particular value. This particular value is known as the *most probable value*.

(ii) **Calculation :** For this speed, the value of $f(v)$ is maximum. So using (19) and concept of maxima and minima, we have

$$
\frac{d}{dv} f(v) = 0
$$
\n
$$
\Rightarrow 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \left[2ve^{-\frac{mv^2}{2k_B T}} - \frac{2mv^3}{2k_B T}e^{-\frac{mv^2}{2k_B T}}\right] = 0
$$
\n
$$
\Rightarrow 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} 2ve^{-\frac{mv^2}{2k_B T}} \left[1 - \frac{mv^2}{2k_B T}\right] = 0.
$$

This gives

Either
$$
v = 0
$$
 or, $e^{\frac{-mv^2}{2k_B T}} = 0 \implies v = \infty$ or, $1 - \frac{mv^2}{2k_B T} = 0$

$$
\Rightarrow
$$
 v = 0, v $\rightarrow \infty$, or v = $\sqrt{\frac{2k_BT}{m}}$

where $v = 0$ and $v \rightarrow \infty$ corresponds to minimum value of $f(v)$.

So
$$
v_{mp} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}
$$
...(20)

- (c) The rms speed $(v_{r.m.s})$:
- **(i) Definition :** It is the speed observed during the experiments and is given by

(ii) Calculation : Now
$$
\overline{v}^2 = \int_0^{\infty} v^2 f(v) dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^{\infty} v^4 e^{-\frac{mv^2}{2k_B T}} dv
$$

\nUsing $\int_0^{\infty} x^n e^{-ax^2} dx = \frac{\frac{n+1}{2}}{\frac{2n+1}{2n}},$ we have
\n $2a^{\frac{n}{2}}$
\n $\therefore \qquad \overline{v}^2 = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{\left(5/2\right)}{2\left(\frac{m}{2k_B T}\right)^{5/2}} = \frac{3k_B T}{m}$
\nSo $\boxed{v_{rms} = \sqrt{\overline{v}^2} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}}$... (22)
\n \therefore Consider a collection of molecules of an ideal case, it is not possible to find

Problem : Consider a collection of molecules of an ideal gas at temperature T. The ratio of the rms speed to the most probable speed of the molecule is **[IISc 2009]**

(a)
$$
\sqrt{3}: \sqrt{2}
$$
 (b) $\sqrt{3}: \sqrt{8}$ (c) 3:8 (d) 3:2
\n**Soln.** $\frac{v_{\text{r.m.s.}}}{v_p} = \frac{\sqrt{3RT/M}}{\sqrt{2RT/M}} = \frac{\sqrt{3}}{\sqrt{2}}$.
\n**Correct option is (a)**

Problem : Three closed vessels A, B and C at the same temperature T and contain gases which obey the Maxwellian distribution of velocities. Vessels A contains only $\rm O_2$, B only $\rm N_2$ and C a mixture of equal quantities of $\rm O_2$ and N₂. If the average speed of the O₂ molecules in vessel A is v_1 , that of the N₂ molecules in vessel B is v_2 , the average speed of the O_2 molecules in vessel C is

(a)
$$
(v_1 + v_2)/2
$$
 (b) v_1 (c) $(v_1 v_2)^{1/2}$ (d) $\sqrt{3k_B T/M}$

Soln. The average speed of molecules of an ideal gas is given by

$$
\langle v \rangle = \sqrt{\frac{8RT}{\pi M}} i.e., \langle v \rangle \propto \sqrt{T}
$$
 for same gas.

Since temperature of A and C are same, average speed of O_2 molecules will be equal in A and C i.e., v_1 .

Correct option is (b)

Problem : This problem is a multiple select question (MSQ).

- Let $\overline{\nu}$, $\overline{\nu}_p$ and $\overline{\nu}_{rms}$ respectively denote the mean speed, root mean square speed and most probable speed of the molecules in an ideal monoatomic gas at absolute temperature T. The mass of a molecule is *m*. Then,
- (a) no molecule can have a speed greater than $\sqrt{2}$ v_{ms}
- (b) no molecule can have a speed less than $v_p/\sqrt{2}$
- (c) $V_p < \overline{V} < V_{rms}$
- (d) the average kinetic energy of a molecule is $\frac{3}{2}mv_p^2$ $\frac{2}{4}mv_p^2$
- **Soln.** The molecules can possess any value of speed lies from zero to infinity. Hence options (a) and (b) both are incorrect.

Moreover, we know that,

$$
v_{\text{rms}} = \sqrt{\frac{3RT}{M}}, \overline{v} = \sqrt{\frac{8}{\pi} \cdot \frac{RT}{M}} = \sqrt{\frac{2.5RT}{M}} \text{ and } v_p = \sqrt{\frac{2RT}{M}}
$$

From these expressions we can see that, v_p

Secondly,
$$
v_{\text{rms}} = \sqrt{\frac{3}{2}} v_p
$$

and average kinetic energy of a gas molecule

$$
= \frac{1}{2} m v_{\rm rms}^2 = \frac{1}{2} m \left(\sqrt{\frac{3}{2}} v_p \right)^2 = \frac{3}{4} m v_p^2.
$$

Correct options are (c, d)

Comparison of the Different Speeds

We know that,

$$
v_{rms} = \sqrt{\frac{3RT}{M}}, \quad v_{mp} = \sqrt{\frac{2RT}{M}}, \quad v_{avg} = \sqrt{\frac{8RT}{\pi M}}
$$

Clearly, $v_{rms} : v_{mp} : v_{avg} = \sqrt{3} : \sqrt{2} : \sqrt{\frac{8}{\pi}}$
 $= 1.732 : 1.414 : 1.596$

So, $v_{rms} > v_{avg} > v_{mp}$

The graph representing v_{rms} , v_{avg} , v_{mp} is

 $\bf Problem:$ If $\rm C_{r.m.s.}$ C and $\rm C_m$ denote respectively the r.m.s speed, average speed and most probable speed molecules in a gas obeying Maxwell-Boltzmann distribution law for the molecular speeds, then **[B.H.U-2011]**

(a)
$$
C_m > \overline{C} > C_{r.m.s}
$$
 (b) $\overline{C} > C_{r.m.s} > C_m$ (c) $C_{r.m.s} > \overline{C} > C_m$ (d) $C_{r.m.s} > C_m > \overline{C}$

Soln. We know that,

$$
C_{\text{r.m.s}} = \sqrt{\frac{3RT}{M}}, \overline{C} = \sqrt{\frac{8}{\pi} \frac{RT}{M}} \text{ and } C_m = \sqrt{\frac{2RT}{M}}
$$

$$
\therefore C_{\text{r.m.s}} : \overline{C} : C_m = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.732 : 1.596 : 1.414
$$

$$
\therefore C_{\text{r.m.s}} > C > C_m
$$

Correct option is (c)

Speed Distribution of the Same Gas at Different Temperature

The speed distribution graphs for the same gas at two different temperatures T_1 and T_2 (> T_1) is given by :

The reasons for this nature of the graphs are :

- (a) Since speed varies proportional to the square root of the temperature, the increase in the temperature causes the greater fraction of molecules to have more value of speed. This causes the broadening of the graph.
- (b) Since the graph under the curve is unity, the broadening of the curve, on increasing the temperature, falls the curve's peak down.

Maxwellian Speed Distribution Function in Different Dimensions

The Maxwellian speed distribution function in different dimensions is given by :

(a) In three dimension :
$$
f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}}
$$

\n(b) In two dimension : $f(v) = 2\pi \left(\frac{m}{2\pi k_B T}\right)^{2/2} v e^{-\frac{mv^2}{2k_B T}}$
\n(c) In one dimension : $f(v) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv^2}{2k_B T}}$ **ENDCAVOUR**

 $(2\pi\kappa_B T)$
As we did for the 3-dimensions, we can also calculate different speeds in other dimension as well. Using the Maxwell-Boltzmann speed distribution functions in different dimensions, we are getting the following values of the various speeds as :

Problem : Electrons of mass *m* in a thin, long wire at a temperature *T* follow a one-dimensional Maxwellian velocity distribution. The most probable speed of these electrons is, [JEST 2015] distribution. The most probable speed of these electrons is,

(a)
$$
\sqrt{\left(\frac{kT}{2\pi m}\right)}
$$
 (b) $\sqrt{\left(\frac{2kT}{m}\right)}$ (c) 0 (d) $\sqrt{\left(\frac{8kT}{\pi m}\right)}$

Soln. The one-dimensional Maxwellian distribution for speed is

$$
f(v) = 2\left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv^2}{2k_B T}}; \ 0 < v < \infty
$$

For most probable speed $(v = v_p)$, we have

$$
\left. \frac{d}{dv} f(v) \right|_{v=v_p} = 0 \Rightarrow v_p = 0.
$$

Correct option is (c)

Maxwell Boltzmann Velocity Distribution Function

Till now, we have studied about the distribution of speeds among the molecules. Now, we will study about the same thing in terms of velocity distribution.

(a) In one dimension :

The velocity distribution function (say in *x*-direction) is given by

$$
f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{\frac{-mv_x^2}{2k_B T}}, -\infty < v_x < \infty
$$
 ... (23)

(i) The average velocity : It is given by

$$
\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x) dv_x = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_{-\infty}^{\infty} v_x e^{\frac{-mv_x^2}{2k_B T}} dv_x
$$

Using $\int_{-a}^{a} f(x) dx = 0$ if $f(-x) = -f(x)$, we have

$$
\langle v_x \rangle = 0
$$

This shows that molecules are distributed uniformly and moving randomly in a gas.

(ii) The most probable velocity :

For this, we have

$$
\left. \frac{d}{dv_x} f(v_x) \right|_{v_x = (v_x)_p} = 0
$$

 \Rightarrow $(v_x)_p = 0$

(iii)The rms velocity : It is given by

$$
\left(v_x\right)_{rms}=\sqrt{\left}
$$

Now $\langle v_x^2 \rangle = \int v_x^2 f(v_x) dx$ ∞ $=\int\limits_{-\infty}$

$$
= \left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_{-\infty}^{\infty} v_x^2 e^{\frac{mv_x^2}{2k_B T}} dv_x
$$

$$
= \frac{k_B T}{m}
$$

$$
\therefore \qquad (v_x)_{rms} = \sqrt{\frac{k_B T}{m}}
$$

Hence, the rms velocity is same as rms speed. Similarly we can calculate in *y* and *z*-axes and we will get the same result as all the directions are identical in nature.

(b) In two dimensions : The velocity distribution is given by

$$
f(v_x, v_y) = f(v_x) f(v_y)
$$

= $\left(\frac{m}{2\pi k_B T}\right)^{2/2} e^{\frac{-m}{2k_B T}(v_x^2 + v_y^2)}, -\infty < v_x, v_y < \infty$... (24)

(i) The average velocity : It is given by

$$
\langle \vec{v} \rangle = \langle v_x \rangle i + \langle v_y \rangle \hat{j}
$$

\nwhere $\langle v_x \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_x f(v_x, v_y) dv_x dv_y = \int_{-\infty}^{\infty} v_x f(v_x) dv_x \int_{-\infty}^{\infty} f(v_y) dv_y$
\n
$$
= 0 \times 1 = 0 \qquad \left[\because \int_{-\infty}^{\infty} f(v_y) dv_y = 1 \right]
$$

\nSimilarly, $\langle v_y \rangle = 0$

Similarly, $\langle v_y \rangle = 0$ $\binom{y}{}$ $\therefore \langle \vec{v} \rangle = 0$ $\rightarrow \overrightarrow{a}$

(ii) The most probable velocity : It is given by

$$
\vec{v}_p = (v_x)_p \hat{i} + (v_y)_p \hat{j}
$$
\nwhere $\frac{d}{dv_x} f(v_x, v_y) \Big|_{(v_x)_p} = 0 = \frac{d}{dv_y} f(v_x, v_y) \Big|_{(v_y)_p}$
\n \Rightarrow $(v_x)_p = (v_y)_p = 0$
\n \therefore $\vec{v}_p = \vec{0}$

(iii) The r.m.s velocity : It is given by

$$
v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\langle v_x^2 \rangle + \langle v_y^2 \rangle}
$$

Now, $\langle v_x^2 \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_x^2 f(v_x, v_y) dv_x dv_y$

$$
= \int_{-\infty}^{\infty} v_x^2 f(v_x) dv_x \int_{-\infty}^{\infty} f(v_y) dv_y
$$

$$
= \frac{k_B T}{m} \times 1 = \frac{k_B T}{m}
$$

Similarly, $\langle v_y^2 \rangle = \frac{k_B T}{m}$
 $\therefore \qquad v_{rms} = \sqrt{\frac{2k_B T}{m}}$

(c) In three dimension :

The velocity distribution function is

$$
f(v_x, v_y, v_z) = f(v_x) f(v_y) f(v_z)
$$

= $\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{\frac{-m}{2k_B T}(v_x^2 + v_y^2 + v_z^2)}, -\infty < v_x, v_y, v_z < \infty$... (25)

As we have done in last two cases, we can calculate the following :

(i) The average velocity :

$$
\langle \vec{v} \rangle = 0
$$

(ii) The most probable velocity :

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

(iii)The rms velocity :

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

(d) Other quantities :

(i)
$$
\langle v_x^a v_y^b v_z^c \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_x^a v_y^b v_z^c f(v_x, v_y, v_z) dv_x dv_y dv_z
$$

\n
$$
= \int_{-\infty}^{\infty} v_x^a f(v_x) dv_x \int_{-\infty}^{\infty} v_y^b f(v_y) dv_y \int_{-\infty}^{\infty} v_z^c f(v_z) dv_z
$$
\n
$$
= \langle v_x^a \rangle \langle v_y^b \rangle \langle v_z^c \rangle
$$
\n...(26)

 $= 0$ if at least one out of *a*, *b* or *c* is odd.

Problem : A classical gas of molecules each of mass m, is in thermal equilibrium at the absolute temperature, T. The velocity components of the molecules along the Cartesian axes are v_x , v_y and v_z . The mean value of $(v_x + v_y)^2$ is:

(a)
$$
\frac{k_B T}{m}
$$
 (b) $\frac{3}{2} \frac{k_B T}{m}$ (c) $\frac{1}{2} \frac{k_B T}{m}$ (d) $\frac{2k_B T}{m}$
\n**Soln.** $\langle (v_x + v_y)^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + 2 \langle v_x v_y \rangle$
\nPutting $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{k_B T}{m}$ $\left[\because \frac{1}{2} m v^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) = \frac{3}{2} k_B T \right]$
\nand $\langle v_x v_y \rangle = 0$
\nSo, $\langle (v_x + v_y)^2 \rangle = \frac{k_B T}{m} + \frac{k_B T}{m} + 0 = \frac{2k_B T}{m}$
\nCorrect option is (d)

Problem : A gas of molecules each having mass 'm' is in thermal equilibrium at a temperature T. Let v_x , v_y , v_z to be the

Cartesian components of velocity, \vec{v} , of a molecule. The mean value of $(v_x - \alpha v_y + \beta v_z)^2$ is:

(a)
$$
\left(1+\alpha^2+\beta^2\right)\frac{k_B T}{m}
$$
 (b) $\left(1-\alpha^2+\beta^2\right)\frac{k_B T}{m}$ (c) $\left(\beta^2-\alpha^2\right)\frac{k_B T}{m}$ (d) $\left(\alpha^2+\beta^2\right)\frac{k_B T}{m}$

Soln. From Maxwell-Boltzmann's distribution, we have

$$
\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{k_B T}{m} \text{ and } \langle v_x y_y \rangle = \langle v_y v_z \rangle = \langle v_z v_x \rangle = 0
$$

So,
$$
\langle (v_x - \alpha v_y + \beta v_z)^2 \rangle = (1 + \alpha^2 + \beta^2) \frac{k_B T}{m}
$$

Correct option is (a)

Problem : Let v_x , v_y , and v_z denote the components of the velocity along *x*-,*y*-, and *z*- directions, respectively, of an ideal gas particle. At the absolute temperature T, the average value of the product $v_x^2 v_y^2 v_z$ ² is proportional to

(a) T (b)
$$
T^{3/2}
$$
 (c) T^3 (d) T^6

Soln. The law of equipartition gives

$$
\left\langle \frac{1}{2}mv_x^2 \right\rangle = \left\langle \frac{1}{2}mv_y^2 \right\rangle = \left\langle \frac{1}{2}mv_z^2 \right\rangle = \frac{1}{2}k_BT
$$

\n
$$
\left\langle v_x^2 \right\rangle = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle = \frac{k_BT}{m}
$$

\n
$$
\left\langle v_x^2 v_y^2 v_z^2 \right\rangle = \left\langle v_x^2 \right\rangle \left\langle v_y^2 \right\rangle \left\langle v_z^2 \right\rangle = \left(\frac{k_BT}{m}\right)^3 \propto T^3
$$

\nCorrect option is (c)

Correct option is (c)

Problem : A gas, the molecules of which have mass m, is at equilibrium at absolute temperature T. The root-meansquare of the relative velocity between any two molecules of the gas is:

(a)
$$
\sqrt{4k_B T / \pi m}
$$
 (b) $\sqrt{3k_B T / 2m}$ (c) $\sqrt{3k_B T / m}$ (d) $\sqrt{6k_B T / m}$

Soln. Relative velocity of two gas molecule is

Relative velocity of two gas molecule is
\n
$$
\vec{v}_r = \vec{v}_1 - \vec{v}_2
$$
\n
$$
\therefore \qquad v_r^2 = v_1^2 + v_2^2 - 2\vec{v}_1 \cdot \vec{v}_2
$$
\n
$$
\Rightarrow \qquad \left\langle v_r^2 \right\rangle = \left\langle v_1^2 \right\rangle + \left\langle v_2^2 \right\rangle - 2(\vec{v}_1 \cdot \vec{v}_2) = \frac{3kT}{m} + \frac{3kT}{m} - 0 = \frac{6kT}{m}
$$

where we have used $\langle \vec{v}_1 \cdot \vec{v}_2 \rangle = 0$

$$
\therefore \qquad (v_r) = \sqrt{\langle v_r^2 \rangle} = \sqrt{6k_B T/m}.
$$

Correct option is (d)

Problem : Suppose you measured *v* x (the *x*-component of the velocity) of every atom in a one-litre can of helium gas (⁴He), kept in equilibrium at 300 K and at atmospheric pressure, at a particular instant of time. The

standard deviation $\sqrt{\langle v_x^2 - \langle v_x \rangle^2}$ in the measurement is approximately equal to (a) 450 m/s (b) 1120 m/s (c) 1400 m/s (d) 800 m/s (e) 14000 m/s

Soln. The average velocity is given by $\langle v_x \rangle = 0$

$$
\sqrt{\langle V_x^2 \rangle - \langle V_x \rangle^2} = \sqrt{\langle V_x^2 \rangle}
$$

= $\sqrt{\frac{1}{3} \langle V^2 \rangle} = \sqrt{\frac{1}{3} \times \frac{3RT}{M}} = \sqrt{\frac{RT}{M}}$
= $\sqrt{\frac{8.314 \times 300}{4 \times 10^{-3}}} \approx 800 \text{ m/s.}$

Correct option is (d)

Problem : If energy (\in) distribution formula for an ideal gas in thermal equilibrium at temperature T is given by

 $dN_{\epsilon} \propto \epsilon^{j} e^{-\epsilon/k_{B}T} d \epsilon$ (where j is a real number), then the velocity distribution of the system is proportional to

(a) $v^2 e^{-mv^2/2k_B T} dv$ (b) $v^{2j} e^{-mv^2}$ $v^{2j} e^{-mv^2/2k_B T} dv$ (c) $v^{2j-1} e^{-mv^2/2k_B T} dv$ (d) $v^{2j+1} e^{-mv^2}$ $v^{2j+1} e^{-mv^2/2k_B T} dv$ [**H.C.U.-2016**]

Soln. Given : $dN_{\varepsilon} \propto \varepsilon^{j} e^{-\varepsilon/k_{B}T} d\varepsilon$

We know that the molecules of an ideal gas do not have any potential energy and hence

$$
\varepsilon = \frac{1}{2}mv^2 \implies d\varepsilon = mv dv
$$

\n
$$
\therefore \qquad dN_v \propto \left(\frac{1}{2}mv^2\right)^j e^{-\frac{mv^2}{2k_BT}}(mv dv) \propto v^{2j+1} e^{-\frac{mv^2}{2k_BT}} dv.
$$

\nCorrect option is (d)
\n**APFER**

Degree of Freedom

(a) **Definition :** It is defined as the total number of independent variables required to describe completely the state of motion of a body. It can be calculated as

$$
f=3N-C,
$$

where *N* represents the number of particles [atoms in case of molecules] and *C* represents the number of constraints [bonds or lone pairs in case of molecules].

Different molecules have various types of degree of freedom corresponds to various types of motion they perform like translation, rotation and vibration. When the molecules are at low temperature, they exhibit only translational motion and hence have only translational degree of freedom. When the temperature increases, they also perform rotational motion along with the translational motion and hence possesses degree of freedom corresponds to both type of motion. When the temperature is sufficiently high, the bonds get weaker and causes the molecules to vibrate along with both translational and rotational motion.

The degree of freedom for various molecules can be calculated as :

(a) For monoatomic molecules [e.g., Ar, Xe, Rn, He]. Each molecule contains one atom and has no bond. So, $N = 1$ and $C = 0$. Therefore, $f = 3 \times 1 - 0 = 3$. All these three degree of freedom corresponds to translational degree of freedom.

- **(b)** For diatomic molecules [e.g., O_2 , N_2 , H_2].
	- Since each diatomic molecule contains two atoms, we have $N = 2$.
	- **(i) At low temperature :** The bond between the two atoms remain rigid and hence there is only one constraints.

```
Therefore, f = 3 \times 2 - 1 = 5.
```
Out of these 5, 3 corresponds to translational motion and 2 corresponds to vibration motion.

(ii) At high temperature : The bond between the atoms do not remain rigid causing the atoms to vibrate as well and hence there is no constraints at high temperature.

Therefore, $f = 3 \times 2 - 0 = 6$.

In this 3 corresponds to translational, 2 corresponds to rotation and the remaining 1 corresponds to vibrational motion.

(c) **For linear triatomic molecules** [e.g., CO_2 , N_2O].

Since each linear triatomic molecule has three atoms, we have $N = 3$.

(i) At low temperature : Since there are two bonds, the number of constraints will be two.

```
Therefore, f = 3 \times 3 - 2 = 7.
```
Out of these 7, 3 corresponds to translation, 2 corresponds to rotation [as the molecules are linear] and the remaining 2 are because of vibrational motion. But if the molecules have rigid bonds, these two vibrational degree of freedom are not active.

(ii) At high temperature : The bonds will not remain constraints and hence $C = 0$. Therefore, $f = 3 \times 3 - 0 = 9$.

Out of these 9, 3 corresponds to translation, 2 corresponds to rotation and the remaining 4 corresponds to vibrational mode.

(**d**) **Non-linear triatomic molecules** [e.g., O_3 , H_2O].

Since each non-linear triatomic molecules has three atoms, we have $N = 3$.

(i) At low temperature : The three bonds will behave as three constraints. So, we have $f = 3 \times 3 - 3 = 6$.

The three, here, corresponds to translational and the remaining three corresponds to rotation [as the molecule is non-linear].

(ii) At high temperature : The bonds will not remain constraints. So, we have

```
f = 3 \times 3 - 0 = 9.
The three will corresponds to translation, three to rotational and the remaining three will corresponds
to vibration.
```
In general, the degree of freedom can be distributed as :

(i) At low temperature :

(ii) At high temperature :

Law of Equipartition of Energy

For 1-D, the Maxwell's velocity distribution function is

$$
f(v) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv^2}{2k_B T}}, \ -\infty < v < \infty
$$

So, average kinetic energy is

$$
\overline{E} = \frac{\int_{-\infty}^{\infty} Ef(v) dv}{\int_{-\infty}^{\infty} f(v) dv} = \frac{\int_{-\infty}^{\infty} \frac{1}{2} m v^2 \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{m v^2}{2 k_B T}} dv}{\int_{-\infty}^{\infty} \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{m v^2}{2 k_B T}} dv}
$$
...(27)

$$
= \frac{m}{2} \frac{\int_{-\infty}^{\infty} v^2 e^{-\frac{mv^2}{2k_B T}} dv}{\int_{-\infty}^{\infty} e^{-\frac{mv^2}{2k_B T}} dv} = \frac{m}{2} \frac{\int_{0}^{\infty} v^2 e^{-\frac{mv^2}{2k_B T}} dv}{\int_{0}^{\infty} e^{-\frac{mv^2}{2k_B T}} dv}
$$

Using
$$
\int_{0}^{\infty} x^{n} e^{-ax^{2}} dx = \frac{\left|\frac{n+1}{2}\right|}{2a^{2}},
$$
 we have

$$
\Rightarrow \overline{E} = \frac{m}{2} \frac{\left(\frac{3}{2}\right)^{2} 2\left(\frac{m}{2k_{B}T}\right)^{3/2}}{\left(\frac{1}{2}\right)^{2} 2\left(\frac{m}{2k_{B}T}\right)^{1/2}} = \frac{m}{2} \frac{\frac{1}{2}\sqrt{\pi}}{\sqrt{\pi}} \frac{2k_{B}T}{m}
$$

$$
\Rightarrow \overline{E} = \frac{1}{2}k_{B}T \qquad (28)
$$

(a) Statement : In thermal equilibrium, any degree of freedom (such as component of the position or velocity of a particle) which appears only "quadratically" in the energy has an average energy per molecule of

$$
\frac{1}{2}k_{B}T.
$$

This is the *law of equipartition of energy*.

- **(b) Examples :**
- **(i) A free particle of mass** *m* **moving in** *xy***-plane** The Hamiltonian will be

$$
H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m}
$$

Since there are two quadratic terms, the average thermal energy is

$$
\langle E \rangle = 2 \times \frac{1}{2} k_B T = k_B T
$$

(ii) A free particle rotating in *xy***-plane about** *z***-axis** The corresponding Hamiltonian is

$$
H=\frac{L_z^2}{2I},
$$

where *I* is the moment of inertia of the particle about *z*-axis. Therefore, the average thermal energy is

$$
\langle E \rangle = 1 \times \frac{1}{2} k_B T = \frac{1}{2} k_B T
$$

(iii)A one-dimensional harmonic oscillator in *x***-axis** The corresponding Hamiltonian is

$$
H = \frac{p_x^2}{2m} + \frac{1}{2} k_x^2,
$$

where *k* is the spring's constant.

Therefore, the average thermal energy is

$$
\langle E \rangle = 2 \times \frac{1}{2} k_B T = k_B T
$$

(c) Other statement : The law of equipartition of energy, therefore, can be re-stated as :

"The average energy corresponds to each translational degree of freedom is $\frac{1}{2}$ $\frac{1}{2}k_BT$, corresponds to each

rotational degree of freedom is $\frac{1}{2}$ $\frac{1}{2}k_BT$ and corresponds to each vibrational degree of freedom is k_BT ".

Mathematically,
$$
\langle E \rangle = f_{\text{Translation}} \times \frac{1}{2} k_B T + f_{\text{Rotation}} \times \frac{1}{2} k_B T + f_{\text{Vibration}} \times k_B T
$$
 (29)

- **Problem :** Calculate the average thermal energy of a diatomic molecule in both low temperature and high temperature condition.
- **Soln.** (i) At low temperature, we have $f_{\text{Translation}} = 3$ and $f_{\text{Rotation}} = 2$.

Therefore,
$$
\langle E \rangle = 3 \times \frac{1}{2} k_B T + 2 \times \frac{1}{2} k_B T = \frac{5}{2} k_B T
$$
.

(ii) At high temperature, we have

 $f_{\text{Translation}} = 3$, $f_{\text{Rotation}} = 2$ and $f_{\text{Vibration}} = 1$.

Therefore,
$$
\langle E \rangle = 3 \times \frac{1}{2} k_B T + 2 \times \frac{1}{2} k_B T + 1 \times k_B T
$$

= $\frac{7}{2} k_B T$

Note **:** The formula for average thermal energy per particle as $\overline{2}^{\kappa_{B}}$ $\langle E \rangle = \frac{f}{g} k_B T$ is valid only when there is no vibrational mode.

Problem : A vessel contains a mixture of one mole of oxygen and two moles of nitrogen at 300 K. The ratio of the average rotational kinetic energy per O_2 molecule to per N_2 molecule is

(a) 1 : 1 (b) 1 : 2 (c) 2 : 1

(d) depends on the moment of inertia of the two molecules

- **Soln.** Since both the gases are diatomic, both will have the same number of rotational degree of freedom i.e., two. Therefore, both the gases will have the same average rotational kinetic energy per molecule $=$ $2 \times 1/2$ $k_{_B}T$ or $k_{B}T$. Thus ratio will be 1 : 1. **Correct option is (a)**
- **Problem :** A gas mixture consists of 2 moles of oxygen and 4 moles of argon at temperature T. Neglecting all vibra-

tional modes, the total internal energy of the system is

(a) $4 RT$ (b) 15 RT (c) $9 RT$ (d) 11 RT

Soln. Internal energy of *n* moles of an ideal gas with no vibrational degree of freedom at temperature *T* is given by

$$
U = n \left(\frac{f}{2} RT \right)
$$

where, $f = \text{degree of freedom}$.

 $= 5$ for O_2 and 3 for Ar

Hence, U

$$
U = U_{O_2} + U_{Ar} = 2\left(\frac{5}{2}RT\right) + 4\left(\frac{3}{2}RT\right) = 11 RT.
$$

Correct option is (d)

Problem : In 1-dimension, an ensemble of *N* classical particles has energy of the form $\frac{2}{x}$ 1 $\frac{1}{kx^2}$ $2m$ 2 $E = \frac{p_x^2}{2} + \frac{1}{2}kx$ *m* $=\frac{P_x}{2}+\frac{1}{2}kx^2$. The average

internal energy of the system at temperature *T* is

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

Soln. The given Hamiltonian is

$$
E = \frac{p_x^2}{2m} + \frac{1}{2}kx^2
$$

According to equipartition theorem, the contribution of each quadratic term in Hamiltonian to average

thermal energy is $\frac{1}{2}$ $\frac{1}{2}k_B T$. So the average thermal energy of one particle is

$$
U_1 = \frac{1}{2}k_B T + \frac{1}{2}k_B T = k_B T
$$

 \therefore Average thermal energy of *N*-particle system is

$$
U = N U_{\scriptscriptstyle 1} = N k_{\scriptscriptstyle B} T
$$

Correct answer is (d)

Problem : A system of N classical non-interacting particles, each of mass m, is at a temperature *T* and is confined by the external potential $V(r) = \frac{1}{2} Ar^2$ (where A is a constant) in three dimensions. The internal energy of the system is

(a)
$$
3 N k_B T
$$
 (b) $\frac{3}{2} N k_B T$ (c) $N (2 \text{mA})^{3/2} k_B T$ (d) $N (2 \text{mA})^{1/2} k_B T$

Soln. The Hamiltonian of a classical particle $\frac{2}{1} + \frac{1}{4} + \frac{2}{5}$ $2m$ 2 $H = \frac{p^2}{2} + \frac{1}{2}Ar$ *m*

$$
=\frac{p_x^2+p_y^2+p_z^2}{2m}+\frac{1}{2}A(x^2+y^2+z^2)
$$

Since the Hamiltonian has 6 quadratic term, the internal energy of a particle is $6 \times \frac{1}{2} k_B T = 3k$ $\times \frac{1}{2} k_B T = 3k_B T$

The internal energy of a system of *N* particles $= 3Nk_B T$. **Correct answer is (a)**

Problem : A system of *N* non-interacting classical point particles constrained to move in the two-dimensional surface of a sphere. The internal energy of the system is

(a)
$$
\frac{3}{2} N k_B T
$$
 (b) $\frac{1}{2} N k_B T$ (c) $N k_B T$ (d) $\frac{5}{2} N k_B T$

Soln. Since the particle is moving on two-dimensional surface, its degree of freedom $= 2$ Hence, for *N* non-interacting particle total degree of freedom = 2*N*

Hence, total energy $U = 2N \times \frac{1}{2}$ $U = 2N \times \frac{1}{2} k_B T$

$$
\Rightarrow U = N k_{B} T
$$

Correct option is (c)

Problem : Mean total energy of a classical three-dimensional harmonic oscillator in equilibrium with a heat reservoir at temperature T is:

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

Soln. The Hamiltonian of a three-dimensional harmonic oscillator is

$$
H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \frac{1}{2}k_1x^2 + \frac{1}{2}k_2y^2 + \frac{1}{2}k_3z^2
$$

Since there are six quadratic terms, we have

$$
\langle E \rangle = 6 \times \frac{1}{2} k_B T = 3 k_B T
$$

Correct option is (d)

Problem : A classical ideal gas of atoms with masses *m* is confined in a three-dimensional potential [TIFR 2018]

$$
V(x, y, z) = \frac{\lambda}{2} (x^2 + y^2 + z^2)
$$

at a temperature T . If k_B is the Boltzmann constant, the root mean square (r.m.s.) distance of the atoms from the origin is

(a)
$$
\left(\frac{3k_BT}{\lambda}\right)^{1/2}
$$
 (b) $\left(\frac{3k_BT}{2\lambda}\right)^{1/2}$ (c) $\left(\frac{2k_BT}{3\lambda}\right)^{1/2}$ (d) $\left(\frac{k_BT}{\lambda}\right)^{1/2}$

Soln. The given potential is $V(x, y, z) = \frac{\lambda}{2} (x^2 + y^2 + z^2)$ 2 $V(x, y, z) = \frac{\lambda}{2} (x^2 + y^2 + z^2)$

Using law of equipartition of energy, we have

$$
\left\langle \frac{\lambda}{2} (x^2 + y^2 + z^2) \right\rangle = \frac{3}{2} k_B T
$$

\n
$$
\Rightarrow \frac{\lambda}{2} \langle r^2 \rangle = \frac{3}{2} k_B T
$$

$$
\therefore \qquad r_{\text{r.m.s.}} = \sqrt{\langle r^2 \rangle} = \sqrt{\frac{3k_B T}{\lambda}}.
$$

Correct option is (a)

Molar Specific Heats

(a) **Molar specific heat at constant volume** (C_v) **:** It is given by

$$
C_{v} = \left(\frac{\partial}{\partial T} \left\langle E \right\rangle\right)_{V} \tag{30}
$$

where $\langle E \rangle$ is the average energy of one mole of the substance.

$$
\therefore C_v = f_{\text{Translation}} \times \frac{1}{2} R + f_{\text{Rotation}} \times \frac{1}{2} R + f_{\text{Vibration}} \times R \qquad \qquad \dots (31)
$$

If there is no vibrational mode, we have

$$
f = f_{\text{Translation}} + f_{\text{Rotation}}
$$

$$
\therefore C_v = \frac{f}{2}R \tag{32}
$$

(b) **Molar specific heat at constant pressure** (C_p) **:** For an ideal gas, it is given by

$$
C_p = C_v + R
$$

If there is no vibrational mode, we have

$$
C_p = \left(\frac{f}{2} + 1\right)R \tag{33}
$$

(c) Ratio of specific heats/Adiabatic index () : It is defined as

$$
\gamma = \frac{C_p}{C_v} \tag{34}
$$

ENDEAVOUR If there is no vibrational mode, we have

$$
\gamma = \frac{\left(\frac{f}{2} + 1\right)R}{\frac{f}{2}R} = 1 + \frac{2}{f}
$$
 ... (35)

Problem : For which gas the ratio of specific heats (C_p/C_v) will be largest? [**JEST 2014**]

(a) mono-atomic (b) di-atomic (c) tri-atomic (d) hexa-atomic **Soln.** The ratio of specific heat is

$$
\frac{C_p}{C_v} = \frac{\left(\frac{f}{2} + 1\right)R}{\frac{f}{2}R}
$$
, where *f* is the degree of freedom for the gas
= 1 + $\frac{2}{f}$.

Since *f* is minimum for mono-atomic gas, i.e., $f = 3$, C_p/C_v , will be largest for mono-atomic gas. **Correct option is (a)**

Problem : Consider the CO molecule as a system of two point particles which has both translational and rotational degrees of freedom. Using classical statistical mechanics, the molar specific heat C_v of CO gas is given in terms of the Boltzmann constant k_B by by **[TIFR 2014]**

(a)
$$
\frac{5}{2}k_B
$$
 (b) $2k_B$ (c) $\frac{3}{2}k_B$ (d) $\frac{1}{2}k_B$

Soln. For diatomic molecule, we have

 $f_{\text{translation}} = 3$ and $f_{\text{rotational}} = 2$. The average energy is

$$
\langle U \rangle = \left(\frac{f_{\text{translational}}}{2} + \frac{f_{\text{rotational}}}{2} + f_{\text{Vibrational}} \right) \times k_B T = \frac{5}{2} k_B T.
$$

Therefore,
$$
C_v = \frac{d}{dt} \langle U \rangle = \frac{5}{2} k_B
$$
.

Correct option is (a)

Problem : Consider oxygen gas at room temperature and pressure and assume that only translational and rotational motions of the molecules contribute to the specific heat. If C_{ρ} and C_{ν} denote respectively, specific heats at constant pressure and volume, then the ratio $C_p/C_{\rm V}$ is

(a)
$$
\frac{3}{5}
$$
 (b) $\frac{5}{3}$ (c) $\frac{5}{7}$ (d) $\frac{7}{5}$ [IISc: 2006]

Soln. Since there is no vibrational mode, we have

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

Since oxygen gas molecules are diatomic in nature, there are two degree of freedom associated with rotational motion and three degree of freedom associated with translational motion.

So, total number of degree of freedom associated with motion of diatomic molecule, $f = 5$

So, $\gamma = 1 + \frac{2}{5} = 1.4$ 5 $\gamma = 1 + \frac{2}{5} = 1$ **Correct option is (d)**

to form diatoring molecules while in B they are connected by bonds of finite stiffness. The ratio
heat per molecule at constant volume of gas A to gas B is **[IISc] Problem :** A and B are both classical ideal gases of diatomic molecules. The point-like atoms in A are bonded rigidly to form diatomic molecules while in B they are connected by bonds of finite stiffness. The ratio of the specific

(a) 1 (b) 5/7 (c) 6/5 (d) 3/4

(c)
$$
6/5
$$

$$
324
$$

Soln. (i) For diatomic molecule A

 $f_{\text{translational}} = 3$, $f_{\text{rotational}} = 2$ and $f_{\text{vibrational}} = 0$

$$
\therefore C_v = \left(\frac{f_{\text{translational}}}{2} + \frac{f_{\text{rotational}}}{2} + f_{\text{vibrational}}\right)R = \frac{5}{2}R
$$

(ii) For diatomic molecule B

$$
f_{\text{translational}} = 3
$$
, $f_{\text{rotational}} = 3$ and $f_{\text{vibrational}} = 1$

$$
\therefore C_v = \frac{7}{2}R
$$

Required ratio = $\frac{5}{7}$. 7 \therefore Required ratio = $\frac{1}{2}$

Correct option is (b)

Problem : A rigid triangular molecule consists of three non-collinear atoms joined by rigid rods. The constant pressure molar specific heat (C_p) of an ideal gas consisting of such molecules is (a) 6*R* (b) 5*R* (c) 4*R* (d) 3*R* **Soln.** We know that, $C_V = \left(\frac{f_{\text{Translational}}}{2} + \frac{f_{\text{Rotational}}}{2} + f_{\text{Vibrational}}\right)R$ $V_V = \left(\frac{J\text{Translation}}{2} + \frac{J\text{Rotational}}{2} + f\text{Vibrational}\right)$ For a non-linear rigid triatomic molecule, we have $f_{\text{Translation}} = f_{\text{Rotational}} = 3$, and $f_{\text{Vibrational}} = 0$ \therefore $C_v = 3R$ $\Rightarrow C_p = C_V + R = 4R$ **Correct option is (c)** 5 $\frac{1}{2}R$. If it is not specified whether it is C_P **Problem :** The molar specific heat of a gas as given from the kinetic theory is or C_v , one could conclude that the molecules of the gas. (a) Are definitely monatomic (b) Are definitely rigid diatomic (c) Are definitely non-rigid diatomic (d) Can be monatomic or rigid diatomic. **Soln.** We know that $C_V = \frac{f_{\text{Translation}}}{2} \times R + \frac{f_{\text{Rotation}}}{2} \times R + \frac{f_{\text{Vibration}}}{2} \times R$ and $C_P = C_V + R$ For monoatomic gas, $f_{\text{Translation}} = 3$ and $f_{\text{Rotation}} = f_{\text{Vibration}} = 0$ Therefore, $C_V = \frac{3}{2} R$ and $C_P = \frac{7}{2}$ $C_V = \frac{3}{2}R$ and $C_P = \frac{7}{2}R$ For rigid diatomic gas, $f_{\text{Translation}} = 3$, $f_{\text{Rotation}} = 2$ and $f_{\text{Vibration}} = 0$ Therefore, $C_V = \frac{5}{3} R$ and $C_P = \frac{7}{3}$ $C_V = \frac{3}{2}R$ and $C_P = \frac{7}{2}R$. Therefore, the gas can be monoatomic or rigid-diatomic. **Correct option is (d)** EAVOUR **Mean Free Path** INCETT THE TRITT
In the assumption of kinetic theory of gases, we assumed that the molecules of gas are moving with very high velocity which means that molecules of gas contained in vessel should disappear in no time which is contrary to

actual observation, because of absence of force to restrain their motion. Thus there was a serious objection against the assumption that the molecules of a gas move with large rectilinear velocities. This difficulty was solved by the Clausius who assumed that the molecules of a gas have a small, but finite size. These molecule collide with one another after short intervals resulting in a change in both the magnitude and direction of the velocities of the molecules.

Since there is no force acting on the molecules except during collision, they move in straight lines with constant speeds between two successive collision. Thus the paths of diffierent molecules is a series of short zig-zag paths of different length. These paths of different length are called the *free paths* of the molecule and their mean is called *mean free path*.

(a) The mean free path : It is defined as the average distance travelled by a molecule between two successive collision.

It can be calculated equals to

$$
\lambda = \frac{1}{\sqrt{2} \pi d^2 n}
$$
 ... (36)

where *d* is the diameter of the molecule and *n* is the particle density i.e. number of molecules per unit volume.

$$
\Rightarrow \lambda = \frac{N}{\sqrt{2} \pi d^2 V} \qquad \left[\because \quad n = \frac{N}{V} \right] \qquad \qquad \dots (37)
$$

$$
\Rightarrow \lambda = \frac{k_B T}{\sqrt{2} \pi d^2 P}, \text{ where we have used } PV = N k_B T \qquad \dots (38)
$$

(b) The collision time : It is defined as the time between two successive collision. It is equals to

$$
\tau = \frac{\lambda}{\overline{\nu}} = \frac{1}{\sqrt{2} \pi d^2 n \overline{\nu}} = \frac{k_B T}{\sqrt{2} \pi d^2 P \overline{\nu}}
$$
...(39)

where \overline{v} is the average speed of the molecules

(c) The collision frequency : It is defined as the number of collisions in one second. It is equals to

$$
=\frac{1}{\tau}=\sqrt{2}\,\pi d^2 n\overline{v}
$$
 ... (40)

Problem : Estimate the mean free path of a molecule of air at 27 °C and 1 atm. Model the molecules as sphere with

radius $r = 2.0 \times 10^{-10}$ m.

(a)
$$
5.8 \times 10^{-9}
$$
m (b) 5.8×10^{-8} m (c) 5.8×10^{-10} m (d) 5.8×10^{-7} m
\n**Soln.** Given: $T = 27$ °C = 300 K, $P = 1$ atm = 1.013×10^5 N/m², $r = 2.0 \times 10^{-10}$ m

The mean free path is $\lambda = \frac{R}{\sqrt{2}\pi d^2}$ $k_B T$ d^2P $\lambda = \pi$, where *d* is the diameter of the molecules $= 2r$

$$
\therefore \ \lambda = \frac{k_B T}{4\sqrt{2}\pi r^2 P} = 5.8 \times 10^{-8} \text{ m}
$$

Correct option is (b)

- **Problem :** At what pressure will the mean free path be 50 cm for spherical molecules of radius 3×10^{-10} m? Assume an ideal gas at 20ºC.
- **Soln.** From the expression for the mean free path, we obtain

$$
\frac{N}{V} = \frac{1}{4\pi\sqrt{2}r^2\lambda}
$$
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where '*r*' is the radius of each molecule.

where 'r' is the radius of each molecule.
Combining this with the ideal gas law in the form $PV = Nk_B T$, we have

$$
P = \frac{k_B T}{4\pi\sqrt{2} r^2 \lambda} = \frac{(1.38 \times 10^{-23} \text{ J/K})(293 \text{K})}{4\pi\sqrt{2}(3.0 \times 10^{-10} \text{m})^2 (0.50 \text{ m})} = 5.1 \text{ mPa}
$$

Problem : If the pressure of a gas, at temperature T, in a closed container is decreased then the mean free path of gas molecules will

(a) increase first then decrease (b) decrease

Soln. The mean free path is given by

$$
\lambda = \frac{V}{\sqrt{2}\pi N d^2}
$$

For a closed container, all the quantities, i.e., *N* and *V* will remain same and hence the mean free path will not change.

Correct option is (d)

(c) increase (d) remain the same **[H.C.U.-2016]**

 $\bf{Problem:}$ One mole of an ideal gas with average molecular speed $v_{_0}$ is kept in a container of fixed volume. If the temperature of the gas is increased such that the average speed gets doubled, then

- (a) the mean free path of the gas molecule will increase
- (b) the mean free path of the gas molecule will not change
- (c) the mean free path of the gas molecule will decrease
- (d) the collision frequency of the gas molecule with wall of the container remains unchanged
- **Soln.** The mean free path of the gas molecule is given by

$$
\lambda = \frac{1}{\sqrt{2 \pi d^2 n_v}}
$$
 (where n_v = number of molecules per unit volume)

Since the mean free path is independent of the temperature and of the average speed as well, the mean free path of the gas molecule λ will not changed in a container fixed volume.

Correct answer is (b)

Problem : Two boxes *A* and *B* contain an equal number of molecules of the same gas. If the volumes are *V^A* and

 V_B , and λ_A and λ_B denote respective mean free paths, then

- 12. Assuming the Maxwellian distribution of speeds for molecules of a liquid also, at temperature below the normal boiling point of a liquid
	- 1. molecules with higher speeds escape from the surface of the liquid.
	- 2. molecules with lower speeds escape from the surface
	- 3. average kinetic enegy of the molecules is the liquid increases as evaporation proceeds
	- 4. average kinetic energy decreases with evaporation
	- (a) 2 and 3 (b) 1 and 4 (c) 2 and 4 (d) 1 and 3
- 13. Maxwell's law of distribution of speed show that the number of molecules with average speed is (a) Very small (b) large (c) zero (d) exactly equal to 1.
- 14. A gas of molecules each having mass '*m*' is in thermal equilibrium at a temperature *T*. If v_x and v_y denote the

Cartesian components of velocity *v* \vec{v} of a molecule. The mean value of $(v_x + v_y)^3$ is

(a) 0 (b)
$$
\left(\frac{k_B T}{m}\right)^{3/2}
$$
 (c) $\left(\frac{2k_B T}{m}\right)^{3/2}$ (d) $\left(\frac{3k_B T}{m}\right)^{3/2}$

15. A gas of argon atoms is kept in a container of volume V and pressure P and is in equilibrium with a heat bath at temperature T. The average energy of an argon atom in the gas is:

(a) RT (b)
$$
3k_{B}T
$$
 (c) $\frac{3}{2}k_{B}T$ (d) 3 RT

where $k_{\rm B}$ is Boltzman constant.

- 16. A vessel contains a mixture of one mole of oxygen and two moles of nitrogen at 300 K. The ratio of the average rotational kinetic energy per O_2 molecule to per N_2 molecule is
	- $(a) 1 : 1$
	- (b) $1:2$
	- $(c) 2 : 1$

(d) depends on the moment of inertia of the two molecules

17. Above a temperature T_0 , the specific heat of a certain gas is approximate 3.5R, and is approximately 2.5R

below T_0 . The gas is most likely

(a) oxygen (b) ozone \overrightarrow{R} (c) carbon dioxide (d) argon 18. In low density oxygen gas at low temperature, only the translational and rotational modes of the molecules

In low density oxygen gas at low temperature, only the translational and rotation
are excited. The specific heat per molecule of the gas is

(a)
$$
\frac{1}{2}k_B
$$
 (b) k_B (c) $\frac{3}{2}k_B$ (d) $\frac{5}{2}k_B$

19. What is the mean free time of an oxygen molecule with $v = v_{rms}$ at 27^oC and 1 atm, where the radius of an oxygen molecule can be taken equals to 2.0×10^{-10} m?

(a) 1.2×10^{-10} sec (b) 0.2×10^{-10} sec (c) 0.2×10^{-12} sec (d) 1.2×10^{-12} sec

- 20. The mean free path is (a) Inversely proportional to the pressure (P) (b) directly proportional to the pressure (c) proportional to P^2
	- (d) proportional to P^4
- 21. The mean free path of the particles of a gas at temperature T_0 and pressure p_0 has a value λ_0 . If the pressure is increased to 1.5 $\mathrm{p_{0}}$ and the temperature is reduced to 0.75 $\mathrm{T_{0}}$, the mean free path (a) remains unchanged. (b) is reduced to half (c) is doubled (d) is equal to $1.125 \lambda_0$

