B.Sc. (Honours) Part-I
Paper-IA

Topic: Gaseous State- Maxwell Boltzmann distribution law of velocities and various velocities of molecules

UG
Subject-Chemistry

Dr. Laxman Singh
Asst. Professor
Department of Chemistry
R.R.S. College (PPU)
(Mokama, Patna)
Email:laxmanrsearcher84@gmail.com

The ratio R/N is constant and is known as Boltzmann constant. Its numerical value is 1.38×10^{-16} erg K^{-1} molecule^{-1}.

4.8 MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR SPEEDS

The gas molecules are moving in all possible directions. They collide with one another and also with the walls of the container. As a result of collisions, the speed and direction of the gas molecules are ever changing, *i.e.*, all the molecules in a given sample of gas do not have the same speed.

The distribution of gas molecules among different possible speeds was studied by **Maxwell** and **Boltzmann** using the theory of probability. The results are mathematically expressed as,

$$dNu = 4\pi N\left[\frac{M}{2\pi RT}\right]^{3/2} e^{-\frac{Mu^2}{2RT}} u^2\, du$$

$$= 4\pi N\left[\frac{m}{2\pi kT}\right]^{3/2} e^{-\frac{mu^2}{2RT}} u^2\, du$$

Here, N = Total number of molecules, M = molar mass of gas

This expression gives the number of molecules (dNu) having speed between u and $(u + du)$ at temperature (T).

A plot of fraction of molecules in the speed range $(u + du)$, $\frac{1}{N}\left(\frac{dNu}{du}\right)$ against speed u is:

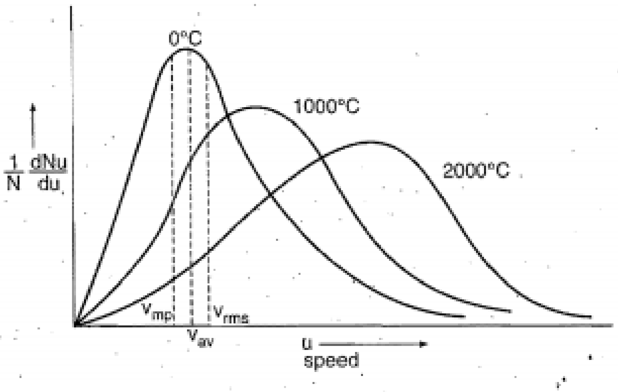

Fig. 4.6

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

Kinds of Molecular Speeds

Molecular speeds are of three types:

(i) The rms speed,
(ii) The average speed and
(iii) The most probable speed

(i) The root mean square speed: The speed in kinetic gas equation, $PV = \frac{1}{3} mnc^2$, is the hypothetical speed possessed by all the gas molecules when the total kinetic energy is equally distributed amongst them. The total kinetic energy of the n molecules of the gas is sum of the kinetic energies of the individual molecules.

Total kinetic energy

$$= \frac{1}{2} mc_1^2 + \frac{1}{2} mc_2^2 + \frac{1}{2} mc_3^2 + \ldots + \frac{1}{2} mc_n^2 \qquad \ldots \text{(i)}$$

Let c be the velocity possessed by each of the n molecules; then,

$$\text{total kinetic energy} = n \times \frac{1}{2} mc^2 \qquad \ldots \text{(ii)}$$

Equating both the equations,

$$n \times \frac{1}{2} mc^2 = \frac{1}{2} mc_1^2 + \frac{1}{2} mc_2^2 + \frac{1}{2} mc_3^2 + \ldots + \frac{1}{2} mc_n^2$$

or $$c^2 = \frac{c_1^2 + c_2^2 + c_3^2 + c_4^2 + \ldots + c_n^2}{n}$$

or $$c = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \ldots + c_n^2}{n}}$$

Thus, rms speed is defined as the square root of the mean of the squares of the speed of all the molecules present in the given sample of the gas. The value of c is determined by using the following expressions:

$$c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

In SI units, the values of R, P, V, M and d used are given below:

(i) $R = 8.314$ J K^{-1} mol^{-1} or $R = 8.314$ kPa dm^3 K^{-1} mol^{-1}
(ii) V of the gas always in litre
(iii) P of the gas in kilopascal (kPa). 1 atm = 101.3 kPa and 1 torr = 0.133 kPa
(iv) M in kg mol^{-1}
(v) d in kg m^{-3}

(ii) Average speed: It is the arithmetic mean of the various speeds of the molecules.

$$\text{Average speed} = \frac{c_1 + c_2 + c_3 + \ldots + c_n}{n}$$

It is equal to $\sqrt{\frac{8RT}{\pi M}}$.

It is related to rms speed by the following relationship:

Average speed = 0.9213 × rms speed

rms speed = 1.085 × average speed

(iii) Most probable speed: This is defined as the speed possessed by maximum number of molecules of a gas at a given temperature.

Note: Root mean square speed explained the non-existence of gases in the atmosphere of moon. Root mean square speed of gases exceeds the escape velocity of moon and hence gases escape from atmosphere of moon against the gravitational barrier of moon.

Maxwell Distribution of Molecular Velocities

As a result of random collisions of gaseous molecules, the molecular velocities keep on changing. Consider a gas molecule of mass m having a velocity component u. Then, the kinetic energy, ε, associated with this velocity component is $\frac{1}{2}mu^2$. The probability that this molecule has its velocity component between u and $u+du$ is given by $p(u)$. In the 19th century, Boltzmann had shown that the probability for a molecule to have an energy ε was proportional to $e^{-\varepsilon/kT}$. It is apparent that

$$p(u) \propto e^{-\varepsilon/kT} \propto e^{-mu^2/2kT} \qquad (\because \ \varepsilon = 1/2\ mu^2)$$

or

$$p(u)du = Ae^{-mu^2/2kT}du \qquad \ldots(22)$$

where A is the constant of proportionality. This constant can be evaluated by requiring that the total probability must be unity. Thus,

$$\int_{-\infty}^{+\infty} p(u)du = A\int_{-\infty}^{+\infty} e^{-mu^2/2kT}\,du = 1 \qquad \ldots(23)$$

The range of integration of velocity component u is $-\infty$ to $+\infty$ since velocity has both magnitude and direction. The integral in Eq. 23 can be easily evaluated. Setting $m/2kT = a$, it is found from calculus that

$$\int_{-\infty}^{+\infty} e^{-au^2}\,du = (\pi/a)^{1/2} = \left(\frac{2\pi kT}{m}\right)^{1/2} \qquad \ldots(24)$$

From Eqs. 23 and 24, $A(2\pi kT/m)^{1/2} = 1$ so that $A = (m/2\pi kT)^{1/2}$ ...(25)

Substituting for A in Eq. 22, we have

$$p(u)du = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mu^2/2kT}du \qquad \ldots(26)$$

Eq. 26 is called the Maxwell distribution of molecular velocities in one dimension. It is easy to derive the Maxwell's distribution of molecular velocities in three dimensions by multiplying the three one-dimension distributions with one another. Thus,

$$p(u,v,w) = p(u)\,p(v)\,p(w) \qquad \ldots(27)$$

where v and w are the velocity components in the other two dimensions.

$$\begin{aligned}\therefore \quad p(u,v,w)du\,dv\,dw &= p(u)du \times p(v)dv \times p(w)dw \\ &= \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m(u^2+v^2+w^2)}{2kT}\right] du\,dv\,dw \qquad \ldots(28)\end{aligned}$$

We are, however, interested in an expression which gives the *fraction of molecules with a velocity between c and $c+dc$* ($c^2 = u^2+v^2+w^2$) regardless of the direction. These are molecules whose velocity points lie within a spherical shell of thickness dc at a distance c. This shell has the volume $4\pi c^2dc$, which is the integral of $dudvdw$ in Eq. 28 over the spherical shell. Hence, we find that

$$p(c)dc = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} c^2 \exp\left(-mc^2/2kT\right)dc \qquad \ldots(29)$$

This result was obtained by Maxwell in 1860 and is called the **Maxwell distribution of molecular velocities.** It is customary to write $p(c)dc$ as dN/N, where N is the total number of gas molecules. The quantity dN/N (or $p(c)dc$) gives the fraction of molecules with velocity between c and $c+dc$. The molecular mass $m = M/N_A$ where M is the molar mass and N_A is the Avogadro's number. Accordingly, Eq. 29 may also be written as

$$p(c)dc = \frac{dN}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} c^2 \exp\left(-\frac{Mc^2}{2RT}\right)dc \qquad ...(30)$$

The Maxwell distribution of molecular velocities is plotted in Fig. 1.

We see that the fraction of molecules having velocities greater than zero increases with an increase in velocity, reaches a maximum and then falls off towards zero again at higher velocities.

The important features of the curves are as follows :

1. The fraction of molecules with too low or too high velocities is very small.

2. There is a certain velocity for which the fraction of molecules is maximum. This is called the most probable velocity.

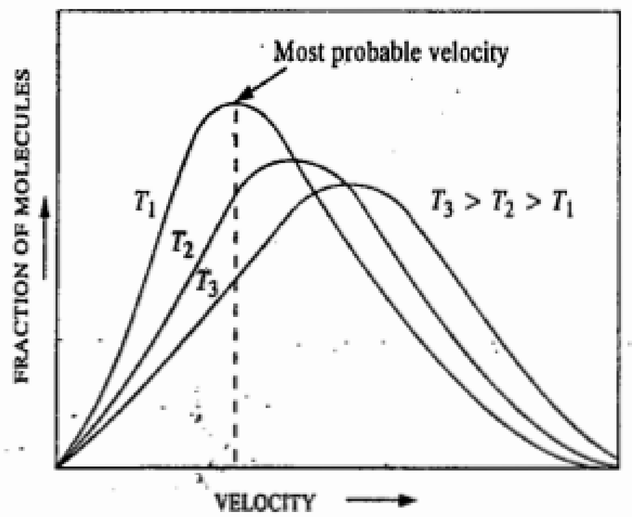

Fig. 1. The Maxwell's distribution of molecular velocities.

The most probable velocity of a gas is the velocity possessed by maximum number of molecules of the gas at a given temperature. It corresponds to the peak of the curve. Its value, at a given temperature, depends upon the volume of the gas.

Effect of Temperature on Distribution of Molecular Velocities. The most probable velocity increases with rise in temperature, as shown in Fig. 1. The entire distribution curve, in fact, shifts to the right with rise in temperature, as shown. The rise in temperature, therefore, increases the fraction of the molecules having high velocities considerably. This can readily be understood from the presence of the factor, $\exp(-mc^2/2kT)$, in Eq. 29. The exponent has a negative sign and the temperature T is in the denominator. The factor, therefore, increases markedly with increases in temperature. This factor is known as the **Boltzmann factor.**

Further, knowing that $\frac{1}{2}mc^2$ is the kinetic energy of one molecule of the gas having velocity c, the factor

$$\exp(-mc^2/2kT) = \exp(-\varepsilon/kT) \qquad ...(31)$$

where ε $(= \frac{1}{2}mc^2)$ gives the kinetic energy per molecule of the gas. The greater the temperature, the greater is the value of ε. Hence, there is rapid increase of the Boltzmann factor with increase in temperature. This conclusion finds application in the theory of reaction rates also.

Maxwell Distribution of Molecular Kinetic Energies. With the help of Eq. 29 it is possible to know how the kinetic energies of translation of molecules are distributed amongst the various molecules. The fraction of molecules having kinetic energies in the range of ε and $\varepsilon + d\varepsilon$, *viz.*, dN_ε/N, can be determined as follows :

$$\varepsilon = \tfrac{1}{2}mc^2 \qquad \text{or} \qquad c^2 = (2\varepsilon/m)$$

$$\therefore \qquad 2cdc = (2/m)(d\varepsilon) \qquad \text{or} \qquad cdc = d\varepsilon/m \qquad ...(32)$$

Thus,

$$c^2dc = c\frac{d\varepsilon}{m} = \left(\frac{2\varepsilon}{m}\right)^{1/2}\left(\frac{d\varepsilon}{m}\right) = \frac{\sqrt{2\varepsilon}}{(m)^{3/2}}d\varepsilon \qquad ...(33)$$

Substituting the above value of c^2dc in Eq. 29, we have

$$p(c)\,dc = \frac{dN_\varepsilon}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{\sqrt{2\varepsilon}}{m^{3/2}}\right)d\varepsilon\ \exp\left(-\frac{\varepsilon}{kT}\right) \qquad ...(34)$$

$$= \frac{2\sqrt{\varepsilon}}{\sqrt{\pi}\,(kT)^{3/2}}\ \exp\left(-\frac{\varepsilon}{kT}\right)d\varepsilon \qquad ...(35)$$

This is the **Maxwell distribution of molecular kinetic energies.**

Example 2. Calculate the fraction of oxygen molecules at 1 atm and 27°C whose kinetic energies lie in the range of $(\varepsilon - 0{\cdot}005\varepsilon)$ and $(\varepsilon + 0{\cdot}005\varepsilon)$.

Solution : According to the Maxwell's distribution of molecular kinetic energies,

$$\frac{dN_\varepsilon}{N} = \frac{2\sqrt{\varepsilon}}{\sqrt{\pi}\,(kT)^{3/2}}\ \exp\left(-\frac{\varepsilon}{kT}\right)d\varepsilon \qquad \text{(Eq. 35)}$$

At 27°C, kinetic energy of the gas is given by

$$\varepsilon = 3/2\ (1{\cdot}38\times10^{-23}\ \text{J K}^{-1})\ (300\ \text{K}) = 6{\cdot}21\times10^{-21}\ \text{J}$$

$$d\varepsilon = (\varepsilon + 0{\cdot}005\varepsilon) - (\varepsilon - 0{\cdot}005\varepsilon) = 0{\cdot}01\varepsilon = 6{\cdot}21\times10^{-23}\ \text{J}$$

Substituting these values in Maxwell's equation (35), we have

$$\frac{dN_\varepsilon}{N} = \left\{\frac{2(6{\cdot}21\times10^{-21}\,\text{J})^{1/2}}{1{\cdot}77[(1{\cdot}38\times10^{-23}\,\text{JK}^{-1})(300\text{K})]^{3/2}}\right\}\times\left\{\exp\left(-\frac{6{\cdot}21\times10^{-21}\,\text{J}}{1{\cdot}38\times10^{-23}\,\text{JK}^{-1}\times300\text{K}}\right)(6{\cdot}21\times10^{-23}\,\text{J})\right\}$$

$$= \frac{2\times0{\cdot}788\times10^{-10}\,\text{J}^{-1}}{1{\cdot}77\times0{\cdot}266\times10^{-30}}\ \exp\,(-1{\cdot}5)\times6{\cdot}21\times10^{-23}\ \text{J}$$

$$= 4{\cdot}647\times10^{-3}$$

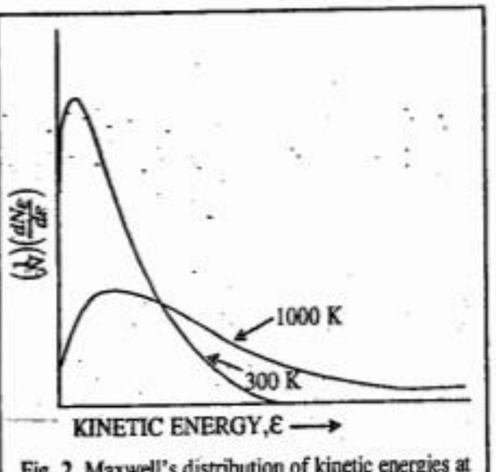

Fig. 2. Maxwell's distribution of kinetic energies at two different temperatures.

The Maxwell distribution of kinetic energies at two different temperatures is shown in Fig. 2 in which the factor $(1/N)\ (dN_\varepsilon/d\varepsilon)$ is plotted against ε. As can be seen, the most probable kinetic energy increases with increase in temperature as expected. The maximum in the probability function corresponds to *the most probable kinetic energy*.

It can be easily shown with the help of Eq. 35 that *(i)* the most probable kinetic energy is given by $kT/2$ per molecule or $RT/2$ per mole of the gas and *(ii)* the average kinetic energy per mole is given by $(3/2)N_AkT=(3/2)RT$. This result is, evidently, in agreement with that obtained from the kinetic theory (Eq. 21).

Types of Molecular Velocities. Three types of molecular velocities are reckoned with in the study of gases. These are : *(i)* the most probable velocity, c_p *(ii)* the average velocity, $<c>$ and *(iii)* the root mean square velocity $<c^2>^{1/2}$.

The **most probable velocity** is defined as the velocity possessed by maximum number of molecules of a gas at a given temperature.

The **average velocity** is given by the arithmetic mean of different velocities possessed by the molecules of the gas at a given temperature. If $c_1, c_2, c_3\ \ldots\ldots\ c_n$ are the individual velocities of the gas molecules and n is their total number, then, average velocity is given by

$$c_1 + c_2 + c_3 + \cdots\cdots\cdots c_n \qquad (36)$$

If, however, c_1, c_2, c_3 .... are the velocities possessed by *groups* of n_1, n_2, n_3 .... molecules of the gas, respectively, then, average velocity is given by

$$<c> = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \cdots\cdots}{n_1 + n_2 + n_3 + \cdots\cdots} \qquad ...(37)$$

The root mean square velocity is defined as the square root of the mean of the squares of different velocities possessed by molecules of a gas at a given temperature. Evidently, the root mean square velocity would be given by

$$<c^2>^{1/2} = \left[\frac{c_1^2 + c_2^2 + c_3^2 + \cdots\cdots c_n^2}{n}\right]^{1/2} \qquad ...(38)$$

where c_1, c_2, c_3 ...... c_n are the individual velocities of n molecules of the gas. Alternatively,

$$<c^2>^{1/2} = \left[\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \cdots\cdots}{n_1 + n_2 + n_3 + \cdots\cdots}\right]^{1/2} \qquad ...(39)$$

where c_1, c_2, c_3, ... are velocities possessed by groups of n_1, n_2, n_3 ...... molecules, respectively.

With the help of the Maxwell equation (Eq. 29), it is possible to derive mathematical expressions for the three types of velocities, *viz.*, the most probable velocity, c_p ; the average velocity, $<c>$ and the root mean square velocity, $<c^2>^{1/2}$. These expressions are as follows :

$$c_p = (2kT/m)^{1/2} = (2RT/M)^{1/2} \qquad ...(40)$$

$$<c> = (8kT/\pi m)^{1/2} = (8RT/\pi M)^{1/2} \qquad ...(41)$$

$$<c^2>^{1/2} = (3kT/m)^{1/2} = (3RT/M)^{1/2} \qquad ...(42)$$

It is found that

$$<c^2>^{1/2} : <c> : c_p = 1{\cdot}00 : 0{\cdot}92 : 0{\cdot}82$$

Derivation of Expressions for c_p, $<c>$ and $<c^2>^{1/2}$

1. Expression for c_p. Differentiating Eq. 29 with respect to c (using dN/N for $p(c)dc$) and setting the result equal to zero, as required for a maximum, we have

$$\frac{d}{dc}\left(\frac{dN}{N}\right) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-mc^2/2kT\right)\left[8\pi c + 4\pi c^2\left(-\frac{mc}{kT}\right)\right] = 0 \qquad ...(43)$$

The factor $(m/2\pi kT)^{3/2}$ is a constant, different from zero. Also, the factor $\exp(-mc^2/2kT)$ is not equal to zero. Hence, the third factor, *viz.*,

$$8\pi c + 4\pi c^2 (-mc/kT) = 0 \qquad ...(44)$$

$$\therefore \qquad c = c_p = (2kT/m)^{1/2} = (2RT/M)^{1/2} \qquad ...(45)$$

2. Expression for $<c>$. The average velocity is given by the expression

$$<c> = \int_0^\infty c\,p(c)dc \qquad ...(46)$$

Substituting the value of $p(c)dc$ from Eq. 29, we have

$$<c> = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty c^3 \exp\left(-\frac{mc^2}{2kT}\right) dc \qquad ...(47)$$

Let $\quad mc^2/2kT = x^2$ so that $c^2 = 2kTx^2/m \qquad ...(48)$

Differentiating both sides, we have

$$dc = 2kT\,xdx/mc \qquad ...(49)$$

Also from Eq. 48, $\quad c = (2kTx^2/m)^{1/2} = (2kT/m)^{1/2}\,x \qquad ...(50)$

Substituting the above value of c in Eq. 49, we have

$$dc = \frac{2kTx\,dx}{m\,(2kT/m)^{1/2}\,x} = \left(\frac{2kT}{m}\right)^{1/2} dx \qquad ...(51)$$

From Eq. 50, $\quad c^3 = (2kT/m)^{3/2} x^3 \qquad ...(52)$

Hence, the expression

$$\int_0^\infty c^3 \exp\left(-\frac{mc^2}{2kT}\right) dc = \int_0^\infty \left(\frac{2kT}{m}\right)^{3/2} x^3\, e^{-x^2} \left(\frac{2kT}{m}\right)^{1/2} dx \qquad ...(53)$$

$$= \left(\frac{2kT}{m}\right)^2 \int_0^\infty x^3\, e^{-x^2} dx = \left(\frac{2kT}{m}\right)^2 \left(\frac{1}{2}\right) \quad \left(\int_0^\infty x^3 e^{-x^2} dx = \frac{1}{2}\right) \qquad ...(54)$$

Thus, from Eqs. 47 and 54,

$$<c> = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{2kT}{m}\right)^2\left(\frac{1}{2}\right) = (8kT/\pi m)^{1/2} = (8RT/\pi M)^{1/2} \qquad ...(55)$$

3. Expression for $<c^2>^{1/2}$. The root mean square velocity is defined as

$$<c^2>^{1/2} = \left\{\int_0^\infty c^2 p(c) dx\right\}^{1/2} \qquad ...(56)$$

From Eq. 29, the expression

$$\int_0^\infty c^2 p(c) dc = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty c^4 \exp\left(-\frac{mc^2}{2kT}\right) dc \qquad ...(57)$$

Let $\quad mc^2/(2kT) = x^2$ so that $c^4 = \left(\frac{2kT}{m}\right)^2 x^4 \qquad ...(58)$

From Eq. 58, $\quad c = \left(\frac{2kT}{m}\right)^{1/2} x$ so that $dc = \left(\frac{2kT}{m}\right)^{1/2} dx \qquad ...(59)$

From Eqs. 57, 58 and 59, it follows that

$$\int_0^\infty c^2 p(c) dc = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{2kT}{m}\right)^2\left(\frac{2kT}{m}\right)^{1/2}\int_0^\infty x^4\, e^{-x^2} dx \qquad ...(60)$$

From the tables of definite integrals, we know that

$$\int_0^\infty x^4 e^{-x^2} dx = (3/8)\pi^{1/2} \qquad ...(61)$$

From the above equations, we have

$$\left\{\int_0^\infty c^2 p(c) dc\right\}^{1/2} = <c^2>^{1/2} = \left(\frac{3kT}{m}\right)^{1/2}$$

$$= \left(\frac{3RT}{M}\right)^{1/2} \qquad ...(62)$$

The molecular distribution of the three types of velocities is shown in Fig. 3

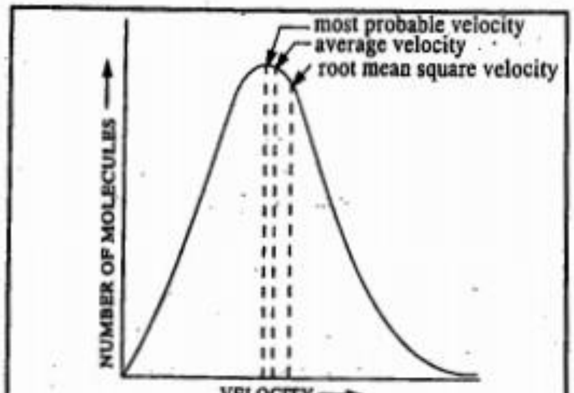

Fig. 3. Molecular distribution of the three types of velocities.

Most Probable speed: This is defined as the speed possessed by maximum number of molecules of a gas at given temperature.

It is equal to $\sqrt{\dfrac{2RT}{M}}$.

This is related to rms speed by the following relationship:

$$\text{Most probable speed} = \left\{\sqrt{\frac{2}{3}}\right\} \text{rms} = 0.816 \text{ rms}$$

or $$\text{rms} = 1.224 \text{ most probable speed}$$

The three kinds of molecular speeds are related to each other as:

Most probable speed : Average speed : rms speed

$$= \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= 1 : 1.128 : 1.224$$

rms speed at any temperature $t°$ C may be related to its value at STP as:

$$c_t = c_0 \sqrt{\frac{(273+t)}{273}} \qquad \text{... (i)}$$

$$c_0 = \sqrt{\frac{3P}{d}} \qquad \text{... (ii)}$$

From eqs. (i) and (ii), we get

$$c_t = \sqrt{\frac{3P}{d}} \sqrt{\frac{(273+t)}{273}}$$

$$= \sqrt{\frac{3P(273+t)}{273d}}$$

Some Essential Points for Distribution of Molecular Speed

(i) The fraction of molecules with very low or very high speeds is very small. Maximum fraction of molecules have speed near to the most probable speed v_{mp}.

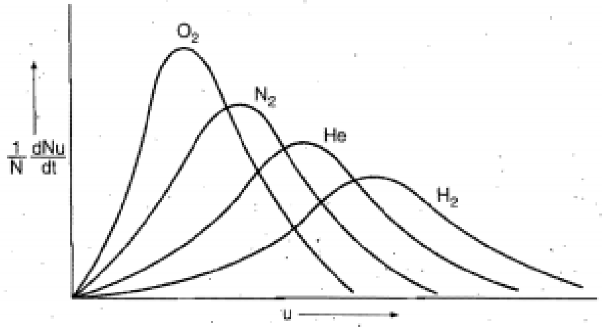

Fig. 4.7 Distribution of molecular speeds of various gases at a constant temperature

(ii) Total area under the curve is a measure of total number of molecules in the collection. Thus, area under the curve remains constant at different temperature.

(iii) Distribution of molecular speed also depends upon the molecular mass of the gas. At similar temperature a heavier gas molecule has a narrow distribution of speed than those of lighter gas molecules.

(iv) The fraction of molecules having speeds greater than minimum goes on increasing with increase in speed. It reaches to a maximum value and then begins to decrease.

(v) As long as temperature of the gas is constant, the fraction having a particular speed remains the same inspite of the fact that the molecules change their speeds due to collisions.

The increase in the temperature of the gas increases the molecular speed. As a result, the most probable speed increases with the increase of temperature and the distribution curve shifts towards right. The general shape of the curve remains the same but the maxima of the curve becomes somewhat flat at a higher temperature, *i.e.*, there is a wider distribution of molecular speeds and the fraction of the molecules having high speeds increases. However, the fraction of molecules possessing most probable speeds decreases with increase in temperature.

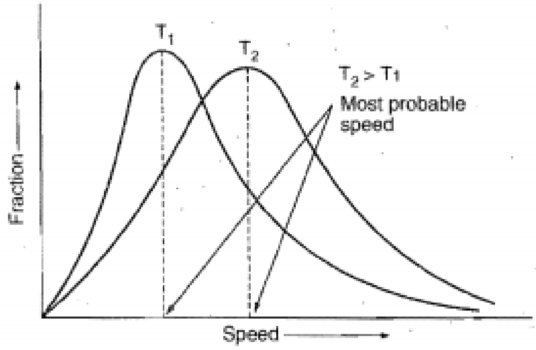

Fig. 4.8

SOME SOLVED EXAMPLES

Example 36. *Calculate the kinetic energy in joule of 8.00 g of methane at 27°C.*

Solution: Number of gram moles of methane $= \frac{8}{16} = \frac{1}{2}$

$$T = (27 + 273) = 300 \text{ K}$$
$$R = 8.32 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Kinetic energy for one gram mole} = \frac{3}{2} RT$$

$$= \frac{3}{2} \times 8.32 \times 300 \text{ J}$$

Thus,

$$\text{kinetic energy for } \frac{1}{2} \text{ gram mole} = \frac{1}{2} \times \frac{3}{2} \times 8.32 \times 300 = 1872 \text{ J}$$

Example 37. *Calculate the average and total kinetic energy of 0.5 mole of an ideal gas at 0°C.*

Solution: Average kinetic energy per molecule of the gas

$$= \frac{3}{2}\frac{R}{N}T$$

$$= \frac{3}{2} \times \frac{8.314 \times 10^7}{6.023 \times 10^{23}} \times 273$$

$$= 5.65 \times 10^{-14} \text{ erg} = 5.65 \times 10^{-21} \text{ J}$$

Total kinetic energy of 0.5 mole of the gas

$$= \frac{3}{2} RT \times 0.5$$

$$= \frac{3}{2} \times 8.314 \times 10^7 \times 273 \times 0.5$$

$$= 1.702 \times 10^{10} \text{ erg} = 1.702 \text{ kJ}$$

Example 38. *Calculate the pressure exerted by* 10^{23} *gas molecules each of mass* 10^{-22} *g in a container of volume 1 litre, the rms speed is* 10^5 *cm* s^{-1}.

Solution: Using kinetic gas equation,

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

Given, $V = 1$ litre = 1000 mL = 1000 cm^3; $n = 10^{23}$; $m = 10^{-22}$ g and $c = 10^5$ cm s^{-1}.

Substituting the values in the above equation,

$$P = \frac{1}{3} \times \frac{10^{-22} \times 10^{23} \times 10^{10}}{1000} = 3.33 \times 10^7 \text{ dyne cm}^{-2}$$

Example 39. *Calculate the root mean square speed of an oxygen molecule at 288 K in SI units.*

Solution: $c = \sqrt{\frac{3RT}{M}}$

$$R = 8.314 \text{kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}, \ T = 288 \text{ K}$$

and $M = 0.032$ kg mol^{-1}

Substituting the values in above equation

$$c = \sqrt{\frac{3 \times 8.314 \times 288}{0.032}} = 473.79 \text{ ms}^{-1}$$

Example 40. *Calculate the root mean square speed of hydrogen molecule at STP.*

Solution: $c = \sqrt{\frac{3PV}{M}}$

$$P = 1 \text{ atm} = 101.3 \text{ kPa}$$

$$V = 22.4 \text{ dm}^3$$

$$M = 2 \text{ g mol}^{-1} = 0.002 \text{ kg mol}^{-1}$$

Substituting the values,

$$c = \sqrt{\frac{3 \times 101.3 \times 22.4}{0.002}} = 1844.91 \text{ ms}^{-1}$$

Alternative method:

$$c = \sqrt{\frac{3RT}{M}}$$

$$R = 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}; \ T = 273 \text{ K};$$

$$M = 0.002 \text{ kg mol}^{-1}$$

Substituting the values,

$$c = \sqrt{\frac{3 \times 8.314 \times 273}{0.002}} = 1845.15 \text{ ms}^{-1}$$

Example 41. *Oxygen at 1 atmosphere and 0°C has a density of* 1.4290 *g* L^{-1}. *Find the rms speed of oxygen molecule.*

Solution: $P = 1 \text{ atm} = 101.3 \times 10^3$ Pa

$$d = 1.4290 \text{ g L}^{-1} = 1.4290 \text{ kg m}^{-3}$$

We know that,

$$c = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 101.3 \times 10^3}{1.4290}} = 461.15 \text{ ms}^{-1}$$

Example 42. *At what temperature will hydrogen molecules have the same root mean square speed as nitrogen molecules at 27°C?*

Solution : $\sqrt{\frac{3RT}{M_{\text{H}}}} = \sqrt{\frac{3R \times 300}{M_{\text{N}}}}$

or $\frac{T}{M_{\text{H}}} = \frac{300}{M_{\text{N}}}$ or $T = \frac{300}{28} \times 2 = 21.43 \text{ K}$

Example 43. *Calculate the root mean square, average and most probable speed of oxygen at 27°C.*

Solution: 27°C = 300 K

$$\text{Root mean square speed} = \sqrt{\frac{3RT}{M}}$$

$R = 8.314 \times 10^7$ erg K^{-1} mol^{-1}; $M = 32$ g mol^{-1}; $T = 300$ K

Substituting the values,

$$= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{32}}$$

$$= 48356 \text{ cm/sec}$$

$$= 483.56 \text{ m/sec}$$

$$\text{Average speed} = \sqrt{\frac{8RT}{\pi M}}$$

$$= \sqrt{\frac{8 \times 8.314 \times 10^7 \times 300 \times 7}{22 \times 32}}$$

$$= 44542 \text{ cm/sec}$$

$$= 445.42 \text{ m/sec}$$

$$\text{Most probable speed} = \sqrt{\frac{2 \times R \times T}{M}}$$

$$= \sqrt{\frac{2 \times 8.314 \times 10^7 \times 300}{32}}$$

$$= 39483 \text{ cm/sec}$$

$$= 394.83 \text{ m/sec}$$

Example 44. *Calculate the average kinetic energy per mole of* CO_2 *gas at 27°C in different units.*

Solution: $\text{KE} = \frac{3}{2} nRT$

$$= \frac{3}{2} \times 1 \times 1.987 \times 300 = 894.15 \text{ cal}$$

$$\text{KE} = \frac{3}{2} nRT$$

$$= \frac{3}{2} \times 1 \times 8.314 \times 300$$

$$= 3741 \text{ J}$$

$$= 3.741 \times 10^{10} \text{ erg}$$

Example 45. *A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of $7.57 \times 10^3\ N\ m^{-2}$. Calculate the root mean square speed and temperature of the gas molecules. If the ratio of most probable speed to the root mean square speed is 0.82, calculate the most probable speed of these molecules at this temperature.*

(IIT 1993)

Solution: Amount of the gas $= \dfrac{2.0 \times 10^{21}}{6.023 \times 10^{23}}$ mole

Given, $V = 1$ litre $= 10^{-3}\ \text{m}^3$; $P = 7.57 \times 10^3\ \text{Nm}^{-2}$, $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$.

Applying $PV = nRT$ or $T = \dfrac{PV}{nR}$

$$T = \frac{10^{-3} \times 7.57 \times 10^3}{\dfrac{2.0 \times 10^{21}}{6.023 \times 10^{23}} \times 8.314} = 274.2 \text{ K}$$

$$\text{rms speed} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 274.2}{28 \times 10^{-3}}} = 494.22 \text{ ms}^{-1}$$

Most probable speed $= 0.8 \times$ rms

$$= 0.8 \times 494.22 \text{ ms}^{-1} = 395.376 \text{ ms}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

16. At what temperature is the root mean square speed of N_2 gas equal to that of propane gas at STP?

(a) 173.7°C (b) 173.7 K (c) 273 K (d) -40°C

[Ans. (b)]

[Hint: $v_{rms}(N_2) = v_{rms}(C_3H_8)$

$$\sqrt{\frac{3RT}{28}} = \sqrt{\frac{3R\ 273}{44}}$$

$$T = 173.7 \text{ K}]$$

17. At what temperature is the kinetic energy of a gas molecule half of its value at 327°C?

(a) 13.5°C (b) 150°C (c) 27°C (d) -123°C

[Ans. (c)]

[Hint: $\text{KE} = \frac{3}{2} RT$

$$\frac{E_1}{E_2} = \frac{\frac{3}{2} RT_1}{\frac{3}{2} RT_2}$$

$$\frac{1}{1/2} = \frac{600}{T_2}$$

$$T_2 = 300 \text{ K}$$

$$t = 27° \text{C}]$$

18. The root mean square speed of molecules of nitrogen gas is v at a certain temperature. When the temperature is doubled, the molecules dissociate into individual atoms. The new rms speed of the atom is:

(a) $\sqrt{2}v$ (b) $2v$ (c) v (d) $4v$

[Ans. (b)]

[Hint: $v_1 = \sqrt{\dfrac{3RT}{M}}$

$$T_2 = 2T,\ M_2 = M/2$$

$$v_2 = \sqrt{\frac{3R \times 2T}{M/2}} = 2v_1]$$

19. The translational kinetic energy of an ideal gas depends only on its:

(a) pressure (b) force

(c) temperature (d) molar mass

[Ans. (c)]

[Hint: $\text{KE} = \frac{3}{2} RT$ ∴ Kinetic energy depends on temperature.]

20. At what temperature is the rms speed of H_2 molecules the same as that of oxygen molecules at 1327°C?

(a) 173 K (b) 100 K (c) 400 K (d) 523 K

[Ans. (b)]

[Hint: $\left(\sqrt{\dfrac{3RT_1}{M_1}}\right)_{H_2} = \left(\sqrt{\dfrac{3RT_2}{M_2}}\right)_{O_2}$

$$\sqrt{\frac{T_1}{2}} = \sqrt{\frac{1600}{32}}$$

$$T_1 = 100 \text{ K}]$$

21. If the temperature of 1 mole of a gas is increased by 50°C, calculate the change in kinetic energy of the system:

(DCE 2006)

(a) 62.32 J (b) 6.235 J (c) 623.5 J (d) 6235.0 J

[Ans. (c)]

[Hint: $E = \frac{3}{2} RT$ (Kinetic energy of 1 mole gas)

$$\Delta E = \frac{3}{2} R(T + 50) - \frac{3}{2} RT$$

$$= \frac{3}{2} R \times 50 = \frac{3}{2} \times 8.314 \times 50$$

$$= 623.55 \text{ J}]$$

22. At same temperature, calculate the ratio of average velocity of SO_2 to CH_4:

(DCE 2006)

(a) 2 : 3 (b) 3 : 4 (c) 1 : 2 (d) 1 : 6

[Ans. (c)]

[Hint: $v_{av} = \sqrt{\dfrac{8RT}{\pi m}}$