

**Lesson 2: Distribution of Molecular speeds: Maxwell-Boltzmann Distribution**

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**Unit-I: Gaseous State**

**Lesson 2: Distribution of Molecular speeds: Maxwell-Boltzmann Distribution**

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## Lesson 2: Distribution of Molecular speeds: Maxwell-Boltzmann Distribution

### • 1.2. Distribution of Molecular Speeds: Maxwell-Boltzmann Distribution

#### 1.2.1 Introduction

In the previous sections, we have already discussed the behavior of molecules of a gas contained in a container i.e., these molecules are in constant random motion, colliding with each other constantly. This implies that these molecules do not have the same speed rather they are moving with different speeds and that is why we talk about average speed or other type of speeds rather than the speed of individual molecule.

**Q: Considering the fact that molecules are in random colliding motion, what should be the probability of finding a molecule with a speed falling in a particular range?**

The solution to this problem was given by James Clerk Maxwell in 1860 and later more rigorously by Ludwig Boltzmann. Collectively, it is known as Maxwell-Boltzmann Distribution.



[http://en.wikipedia.org/wiki/File:James\\_Clerk\\_Maxwell.png](http://en.wikipedia.org/wiki/File:James_Clerk_Maxwell.png)

#### **James Clerk Maxwell (1831-1879):**


He was a well-known mathematician and physicist during 19<sup>th</sup> century. At the early age of his life, he was a shy child and his way of learning things were quite different due to which he faced some problems in his childhood. But, later on he became one of the most brilliant students in his school. His alma maters were University of Edinburgh and University of Cambridge.

He wrote his 1<sup>st</sup> paper at the age of 14, titled "*On the description of oval curves, and those having a plurality of foci*".

He formulates a set of equations describing electricity, magnetism, and optics.

He is recognized for Maxwell's equations, Maxwell distribution, Maxwell's demon, Maxwell's discs, Maxwell speed distribution, Maxwell's theorem and many more.

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	<p><b>Ludwig Boltzmann (1844-1906):</b> He was an Austrian physicist and a great philosopher. His alma mater is University of Vienna. Theoretical physics was his passion and he also taught mathematics, experimental physics in a number of Universities. At the age of 25, he became a Professor of Mathematical Physics at the University of Graz. He is renowned for his contribution in the development of statistical mechanics. He also gave the statistical explanation of the second law of thermodynamics. He is known for Boltzmann constant, Boltzmann equation, Boltzmann distribution, H-theorem, Maxwell-Boltzmann distribution, Stefan-Boltzmann constant and Stefan-Boltzmann law.</p> <p>Despite of so many contributions in the field of science, he faced the harsh criticism of his work due to which he committed suicide.</p>
<p><a href="http://en.wikipedia.org/wiki/Ludwig_Boltzmann">http://en.wikipedia.org/wiki/Ludwig_Boltzmann</a></p>	

This duo derived the following theoretical equation for the distribution of molecular speeds between  $u$  and  $u + du$ , which depends on the temperature and molecular mass of a gas and is given by:

$$F(u^2)du = \frac{dN_u}{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} u^2 \exp\left(-\frac{mu^2}{2kT}\right) du \quad (2.1)$$

$F(u^2)$  = Probability Density for the distribution of molecular speeds

(Note that probability density is a function of  $u^2$  and not  $u$ . Why?)

$N$  = Total number of molecules in the container

$dN_u$  = Number of molecules out of a total number ( $N$ ) of molecules in a gas, having speeds in the range of  $u$  and  $u + du$ .

$\frac{dN_u}{N}$  = fraction of molecules having speeds between  $u$  and  $u + du$  which is directly proportional to  $F(u^2)$ .

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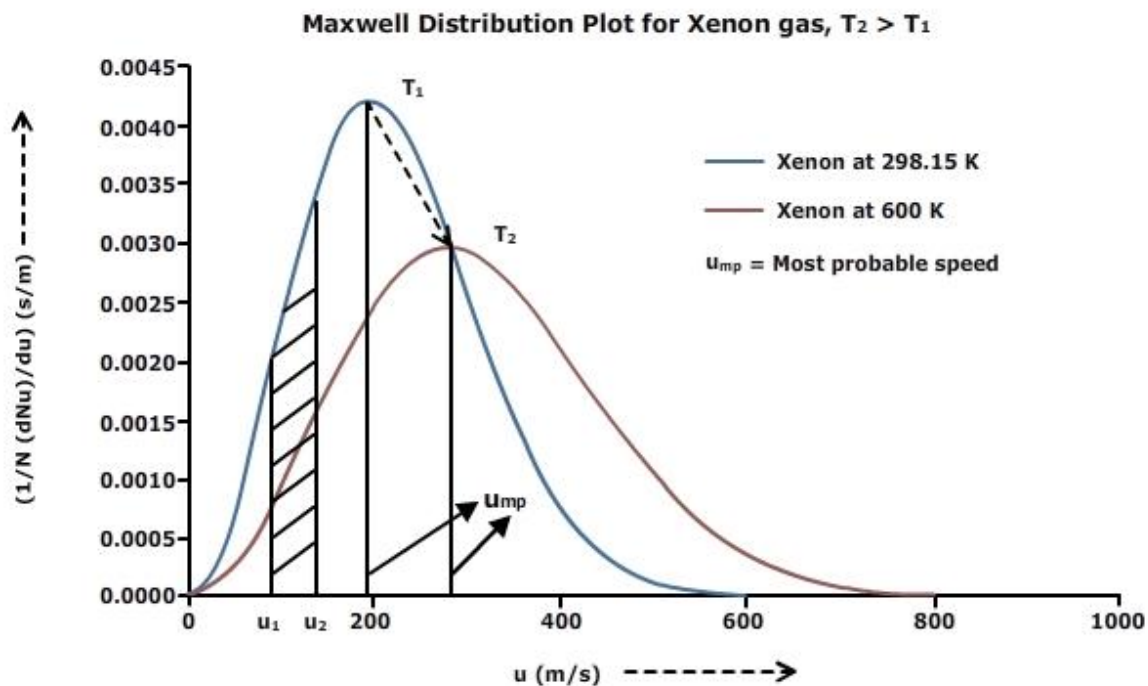
$m$  = Mass of one molecule of a gas

$T$  = Temperature of the gas

The above equation (Eq. 2.1) is known as Maxwell-Boltzmann Distribution Law for molecular speeds. When this equation is divided by  $du$ , we get fraction of molecules in the speed range  $u$  and  $u + du$  per unit width of interval i.e.,

$$F(u^2) = \frac{1}{N} \left( \frac{dN_u}{du} \right) = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} u^2 \exp\left(-\frac{mu^2}{2kT}\right) \quad (2.2)$$

Therefore, the Maxwell-Boltzmann distribution is customarily plotted with the function  $\frac{1}{N} \left( \frac{dN_u}{du} \right)$  as the ordinate (y-axis) and  $u$  as the abscissa (x-axis), as shown in Figure 2.1



**Source: Author, In House ILL**

**Figure 2.1** Maxwell-Boltzmann Distribution plot for the Xenon gas at two different temperatures  $T_1$  &  $T_2$  where  $T_2 > T_1$ . (Figure has been developed in Microsoft Excel by the author, using real values)



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### 1.2.1.1 Key observations regarding Maxwell Boltzmann Distribution

#### Plots

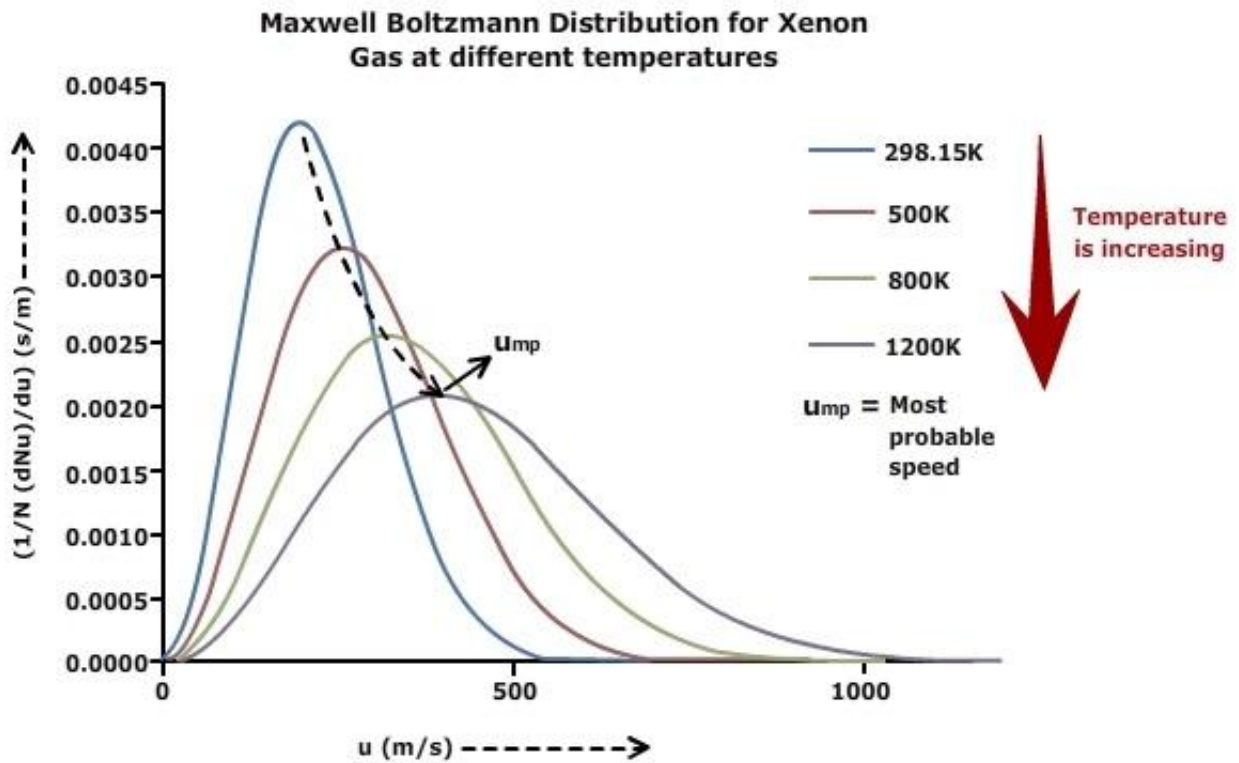
- 1) Near the origin, plot is parabolic in nature due to the factor  $u^2$  dominant in this region.
- 2) At high values of speed, the exponential factor dominates i.e., the function  $\exp\left(-\frac{mu^2}{2kT}\right)$  would fall rapidly at higher values of speed. This factor is known as the **Boltzmann factor**.
- 3) The consequence of above two contrasting behaviors (or factors) makes the product function, a complete distribution function, to have a maxima in the plot.
- 4) This maxima corresponds to a speed known as MOST PROBABLE SPEED,  $u_{mp}$  which will be calculated quantitatively in next section.

### 1.2.1.2 Interpretation of the Maxwell- Boltzmann Distribution Plots

- 1) The probability that a molecule has a speed between any two given values is given by area under the curve between these two values of speed (see shaded area in Fig. 2.1). The total area under the curve is always unity.
- 2) The probability of a molecule being motionless (i.e.,  $u = 0$ ) at any instant is almost zero.
- 3) Plot depicts the fact that chances of finding the molecules with very low or very high speeds are very small.
- 4) The majority of molecules are those which have speeds that are grouped around  $u_{mp}$  i.e., the peak of the curve at any temperature.

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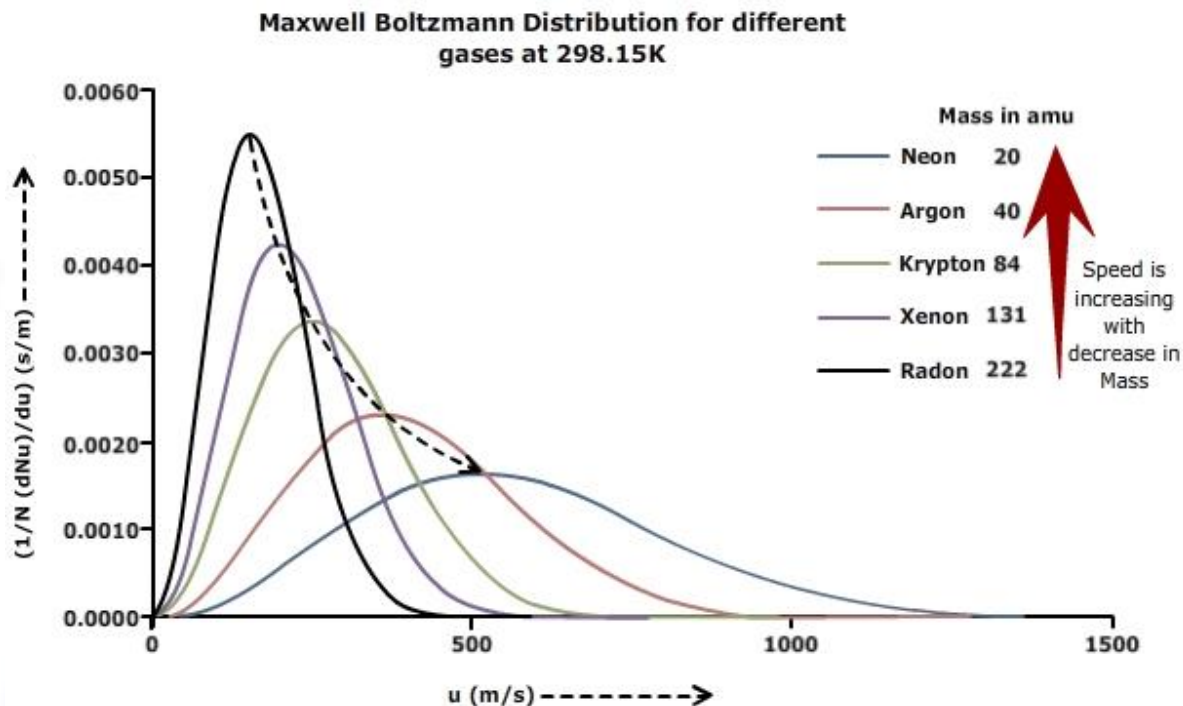
### 1.2.1.3 Effect of Temperature and Mass of a gas on nature of plot



(a)

Source: Author, In House ILL

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Source: Author, In House ILL

**Figure 2.2** Maxwell-Boltzmann Distribution Plot (a) For xenon gas at varying temperatures and (b) For various noble gases at 298.15K temperature. (All figures have been developed in Microsoft Excel by the author, using real values)

### Interpretation of the above Plots

- 1) As depicted by Fig. 2.2(a), with increase in temperature, the probability distribution function broadens i.e., more fraction of molecules falls in higher range of speeds, grouped around  $u_{mp}$ . The curve gets broader with increase in temperature because area under the curve will remain unity even if temperature increases.
- 2) The peak of the plot i.e., maxima shifts to the right as speed increases i.e.,  $u_{mp}$  also increases. This is expected because increase in temperature corresponds to the increase in kinetic energy and subsequently an increase in molecular speed.
- 3) Fraction of molecules having very high speed range increases whereas those with very low speed range decreases.
- 4) **Dependence on mass of the molecules** of a gas can be interpreted by Equation 2.2 that heavier the gas narrower should be the distribution (See Fig.



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2.2(b)). This is expected because average kinetic energy =  $(3/2)kT$  i.e., a constant quantity, dependent on temperature only but average kinetic energy also equal to  $(1/2) m\langle u^2 \rangle$ . Therefore, increase in mass must be compensated by a decrease in mean square speed ( $\langle u^2 \rangle$ ). Hence, at lower speed range distribution functions shows higher peak for heavier gases.

- 5) Equation 2.2 also shows that the distribution of speeds depends collectively on mass and temperature i.e., on the factor  $M/T$ .

**Activity:** Try to plot the distribution for a gas having mass  $M$  and temperature  $T$  and another gas having mass  $2M$  and temperature  $2T$ . See whether the curves overlap or not.



### Think about it?

**At the absolute zero of temperature almost all the molecules have zero kinetic energy. Explain why?**

**Hint:** Use the concept of Maxwell-Boltzmann Distribution of molecular speeds at very low temperatures.

- As temperature is a measure of broadness of speed distribution one can say that, if we, somehow, narrow the distribution to such an extent that the temperature falls to a minimal value then at absolute zero of temperature, the distribution becomes infinitely narrow i.e, almost all the molecules will have zero speed<sup>1</sup>.



### Think about it?

**Why are we talking about distribution of molecular speeds and not velocities? What difference would it make?**

- Speed is the magnitude of velocity. We are always concerned with speed of molecules rather than velocity because many physical properties of gases are dependent only on the magnitude of velocity rather than the direction of motion. Moreover, if instead of speed, the distribution of velocities is studied the nature of distribution would remain the same, with some minor changes, but range of variation of velocity would be between positive value and negative value of scale; whereas for speed it is always greater than zero.

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### Do you know?

It was after almost 100 years of development of Maxwell-Boltzmann Distribution Law, that the experimental verification of this law was done. The experiment was performed by Miller and Kusch (in 1955). The results were in excellent agreement with theoretical ones.

## 1.2.2 Type of Speeds & their evaluation using Maxwell-Boltzmann Distribution

### 1.2.2.1 Most Probable Speed, $u_{mp}$

The speed which most of the molecules possess at any given temperature is known as most probable speed,  $u_{mp}$ . This speed corresponds to the peak of Maxwell-Boltzmann Distribution curve. Since, at the maxima of the curve, the slope is zero, therefore, we can calculate  $u_{mp}$  by putting the first derivative of the plot to zero i.e.

$$\begin{aligned}\frac{dF(u^2)}{du} &= 0 \\ \therefore \frac{dF(u^2)}{du} &= \frac{d}{du} \left[ 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} u^2 \exp\left(-\frac{mu^2}{2kT}\right) \right] = 0 \\ 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \left[ \exp\left(-\frac{mu_{mp}^2}{2kT}\right) \left\{ 2u_{mp} + u_{mp}^2 \left( \frac{-2mu_{mp}}{2kT} \right) \right\} \right] &= 0 \\ \Rightarrow 2u_{mp} + u_{mp}^2 \left( \frac{-2mu_{mp}}{2kT} \right) &= 0 \\ \Rightarrow 2u_{mp} - \frac{mu_{mp}^3}{kT} &= 0 \\ \Rightarrow u_{mp}^2 &= \frac{2kT}{m}\end{aligned}$$

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$$\Rightarrow u_{mp} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} \quad (2.3)$$

### 1.2.2.2 Average Speed, $u_{avg}$

It is the speed possessed by average number of molecules of a gas at a given temperature.

$$\langle u \rangle = \frac{u_1 + u_2 + u_3 + \dots \dots \dots u_N}{N} = \frac{1}{N} \sum_i u_i$$

For very large number of molecules i.e., when N is very large, summation sign can be replaced by integration, such that

$$\begin{aligned} \therefore \langle u \rangle &= \frac{1}{N} \int_0^{\infty} u dN_u = \int_0^{\infty} u \frac{dN_u}{N} = \int_0^{\infty} u F(u^2) du \\ \Rightarrow \langle u \rangle &= \int_0^{\infty} u \left[ 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} u^2 \exp\left(-\frac{mu^2}{2kT}\right) \right] du \\ \Rightarrow \langle u \rangle &= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} u^3 \exp\left(-\frac{mu^2}{2kT}\right) du \end{aligned}$$

Using the following standard definite integral, we can have the solution of above integral:

Standard Definite Integral:

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}} \quad (\text{where, } n \text{ is an odd integer})$$

Therefore, comparing with our integral to be solved,  $n = 1$  &  $a = m/2kT$ , hence,

$$\begin{aligned} \Rightarrow \langle u \rangle &= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \left[ \frac{1!}{2 \left( \frac{m}{2kT} \right)^{1+1}} \right] \\ \Rightarrow \langle u \rangle &= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \left[ \frac{2k^2 T^2}{m^2} \right] \end{aligned}$$

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$$\Rightarrow \langle u \rangle = u_{avg} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \quad (2.4)$$

### 1.2.2.3 Root Mean Square Speed, $u_{rms}$

It is defined as the square root of mean of square of different speeds possessed by molecules of a gas at a given temperature.

$$\langle u \rangle^{1/2} = u_{rms} = \left[ \frac{u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2}{N} \right]^{1/2} = \frac{1}{N} \sum_i u_i^2$$

For very large number of molecules i.e., when N is very large, summation sign can be replaced by integration, such that

$$\therefore u_{rms}^2 = \frac{1}{N} \int_0^{\infty} u^2 dN_u = \int_0^{\infty} u^2 \frac{dN_u}{N} = \int_0^{\infty} u^2 F(u^2) du$$

$$\Rightarrow u_{rms}^2 = \int_0^{\infty} u^2 \left[ 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} u^2 \exp\left(-\frac{mu^2}{2kT}\right) \right] du$$

$$\Rightarrow u_{rms}^2 = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} u^4 \exp\left(-\frac{mu^2}{2kT}\right) du$$

Using the following standard definite integral, we can have the solution of above integral:

Standard Definite Integral:

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \times 3 \times 5 \dots \times (2n-1)}{2^{n+1} a^n} \left( \frac{\pi}{a} \right)^{1/2} \quad (\text{where, } n \text{ is an even integer})$$

Therefore, comparing with our integral to be solved,  $n = 2$  &  $a = m/2kT$ , hence,

$$\Rightarrow u_{rms}^2 = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \left[ \frac{1 \times 3}{2^{2+1} \left( \frac{m}{2kT} \right)^2} \left( \frac{\pi}{m/2kT} \right)^{1/2} \right]$$

$$\Rightarrow u_{rms}^2 = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \left[ \left( \frac{3}{8} \right) \left( \frac{4k^2 T^2}{m^2} \right) \left( \frac{2\pi kT}{m} \right)^{1/2} \right]$$



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$$\Rightarrow u_{rms}^2 = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left[\left(\frac{3 \times 4\sqrt{2\pi}}{8}\right) \left(\frac{kT}{m}\right)^{5/2}\right]$$

$$\Rightarrow u_{rms}^2 = \frac{3kT}{m}$$

$$\Rightarrow u_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} \quad (2.5)$$

### 1.2.2.4 Comparison of the three speeds i.e. $u_{mp}$ , $u_{avg}$ & $u_{rms}$

Using the equations (2.3 to 2.5), we get

$$u_{avg} = \sqrt{\frac{8RT}{\pi M}}; u_{rms} = \sqrt{\frac{3RT}{M}}; u_{mp} = \sqrt{\frac{2RT}{M}}$$

Hence,

$$a) \quad \frac{u_{mp}}{u_{rms}} = \sqrt{\frac{2RT}{M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{2}{3}} = 0.8165 u_{rms}$$

$$b) \quad \frac{u_{avg}}{u_{rms}} = \sqrt{\frac{8RT}{\pi M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{8}{3\pi}} = 0.9216 u_{rms}$$

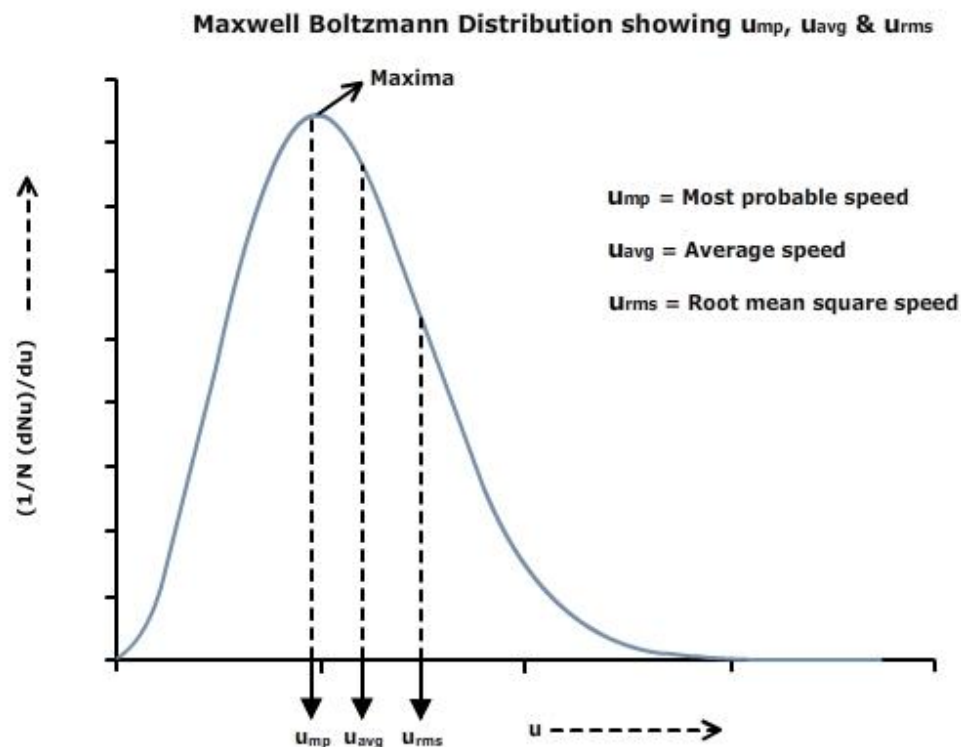
$$\therefore u_{rms} : u_{avg} : u_{mp} = 1 : 0.92 : 0.82$$

Therefore,

$$\therefore u_{rms} > u_{avg} > u_{mp}$$

Please note that all three values are independent of Pressure and are directly proportional to  $T^{0.5}$  and inversely proportional to  $M^{0.5}$ . Figure 2.3 depicts the pictorial representation of all the three speeds viz.  $u_{mp}$ ,  $u_{avg}$  and  $u_{rms}$ .

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Source: Author, In House ILL

**Figure 2.3** Pictorial representation of all three speeds ( $u_{mp}$ ,  $u_{avg}$  and  $u_{rms}$ )



**Think about it?**

**How to evaluate average kinetic energy from Maxwell-Boltzmann distribution of molecular speeds.**

**Hint:**

$$\begin{aligned}
 \langle K.E. \rangle &= \frac{\frac{1}{2}mu_1^2 + \frac{1}{2}mu_2^2 + \frac{1}{2}mu_3^2 + \dots + \frac{1}{2}mu_N^2}{N} = \frac{m}{2N} \sum_i u_i^2 = \frac{m}{2N} \int_0^\infty u^2 dN_u = \frac{m}{2} \int_0^\infty u^2 \frac{dN_u}{N} \\
 &= \frac{m}{2} \int_0^\infty u^2 F(u^2) du = \frac{m}{2} \left( \frac{3kT}{m} \right) = \frac{3}{2} kT \text{ per molecule} = \frac{3}{2} RT \text{ per mole}
 \end{aligned}$$

## **1.2.3. Law of Equipartition of Energy**

### **1.2.3.1 Statement of the law & its example**

The law of equipartition of energy may be stated as:

“If the energy of a molecule can be written in the form of a sum of terms, each of which is proportional to the square of either a velocity component or a coordinate, then the contribution of each of these terms to the average energy is equal to  $(\frac{1}{2})kT$ .”

For example, the average translational energy of a molecule can be calculated with the help of the classical law of equipartition of energy.

$$\langle E_{trans} \rangle = \frac{1}{2}m \langle u^2 \rangle = \frac{1}{2}m(\langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle)$$

$$\therefore \langle E_{trans} \rangle = \langle E_{trans} \rangle_x + \langle E_{trans} \rangle_y + \langle E_{trans} \rangle_z$$

Now, since each term in the above relation is proportional to square of velocity component, according to law of equipartition of energy, each would contribute  $\frac{1}{2}kT$  to total average translational energy. Moreover, since no direction is preferred direction, the velocities along the three axes are equally probable i.e.  $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$  and therefore,

$$\langle E_{trans} \rangle_x = \langle E_{trans} \rangle_y = \langle E_{trans} \rangle_z.$$

Hence,

$$\langle E_{trans} \rangle = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$$

i.e the average translational kinetic energy possessed by the molecules, in each component or per degree of freedom is equal to  $(\frac{1}{2})kT$  per molecule or  $(\frac{1}{2})RT$  per mole.

### **1.2.3.2 Degree of freedom**

Degree of freedom of a molecule may be defined as “the independent number of parameters which must be specified to describe the state or position of the molecule”. For example, pressure, volume, temperature & composition are used to describe the state of the system (Generally used in thermodynamic & phase rule studies) whereas coordinates, angles, bond distances are used to describe the position of a particle. Similarly, we can use the concept of various types of energies possessed by the particles for describing total energy of the

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system. In such a case, degrees of freedom are represented by translational, rotational and vibrational motions of the particles (atoms/molecules).

**Analogy:** To have a better understanding of degrees of freedom one can take this illustration that suppose we want to describe a student's identity then we would need to describe his subject course, then semester, & then his roll number. All these three parameters describe him but it should be noted that all these three parameters are dependent on each other. Just for the sake of understanding, we can take some other parameters to describe his state which are independent of each other e.g., his class roll number, father's name, hostel room number, contact number, facebook profile, twitter profile. etc. Now, one should note that all these parameters would be able to describe



**How many such parameters are available to describe the state of the system?**

- Let a system consists of a gas having **N** molecules then the system would be described by specifying three coordinates of each molecule i.e. a total of **3N** coordinates. Therefore, there are **3N** independent components of the motion, or degrees of freedom available for describing such a system. However, if the system consists of polyatomic molecule, the **3N** coordinates and the components of motion are chosen by describing their Translational, Rotational and Vibrational degrees of freedom.

### • Translational Degrees of Freedom

Translational motion of an atom or a molecule can be ascribed to the translation of its position, which is further described by three coordinates viz. x, y & z (in case of a molecule, position is described by coordinates of center of mass). Thus, all the monoatomic or polyatomic gases have three translational degrees of freedom, possessed in the form of translational kinetic energy

$$\langle E_{trans} \rangle = \frac{1}{2}m \langle u_x^2 \rangle + \frac{1}{2}m \langle u_y^2 \rangle + \frac{1}{2}m \langle u_z^2 \rangle$$

Since each of the terms contains the square of a velocity component, each would contribute  $(\frac{1}{2})kT$  to the average translational energy.

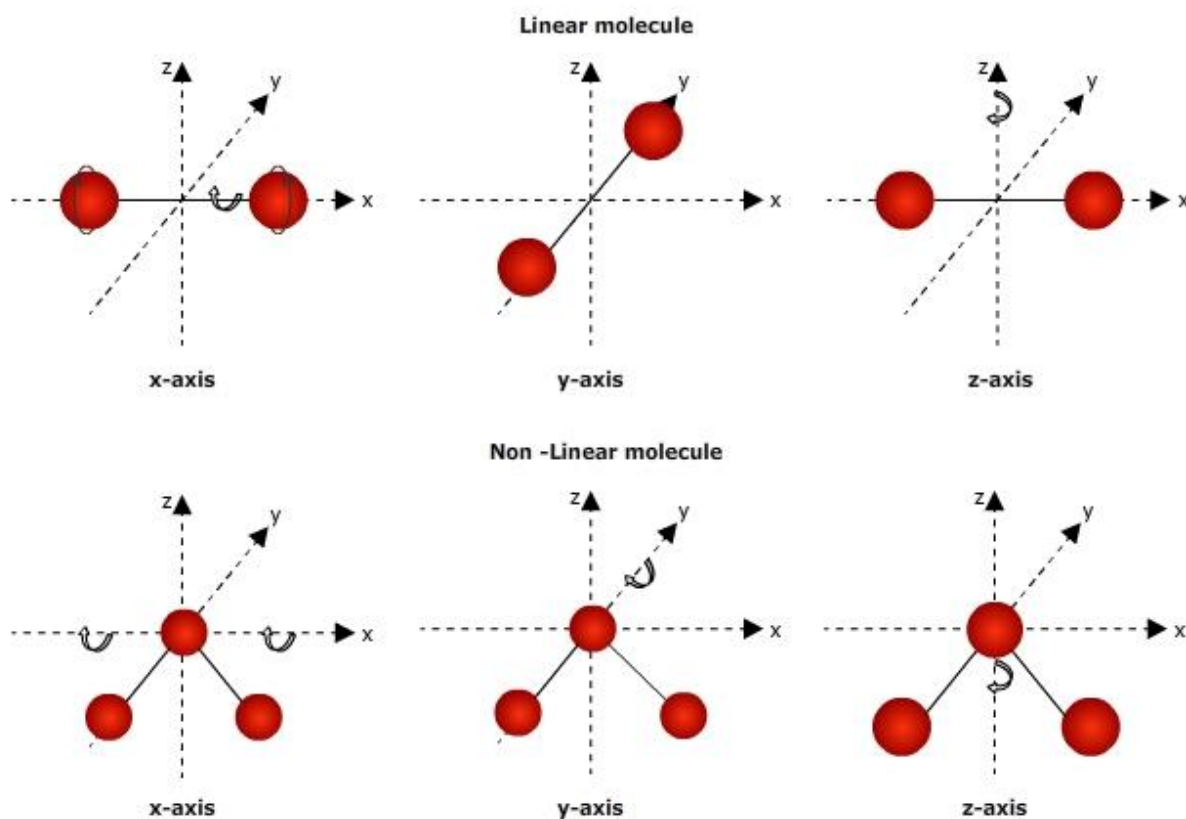
$$\langle E_{trans} \rangle = 3\left(\frac{1}{2}kT\right) \text{ per molecule/atom} \quad (2.6)$$



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- **Rotational Degrees of Freedom**

Representation of axes of rotation: a) linear molecule and b) non-linear molecule



Source: Author, In House ILL

**Figure 2.4** Representation of axes of rotation in a) linear molecule and b) non-linear molecule

Rotational motion of any molecule (Note that Rotational degrees of freedom do not exist for an atom) can be ascribed to its rotation about the axes described by angular coordinates. In case of linear molecules, two angles (rotation about two axes mutually perpendicular to principle axis) are needed to describe the orientation whereas in case of non-linear molecules, three angles (Rotation about all three axes) are needed to describe its orientation (see Figure 2.4).

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Hence, the average rotational energy is given by

$$\langle E_{rot} \rangle = \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2 \quad (\text{For linear molecules})$$

$$\langle E_{rot} \rangle = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2 \quad (\text{For non-linear molecules})$$

where, **I** is the moment of Inertia and  $\omega$  is the angular velocity, both along their respective axis of rotation.

Two things are clear from above equations. Firstly, the number of rotational degrees of freedom in case of linear molecules is two whereas for non-linear molecules it is three. Therefore, all linear molecules such as  $\text{BeH}_2$ ,  $\text{LiH}$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_2$  etc. have 2 rotational degrees of freedom whereas molecules such as  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{C}_6\text{H}_6$ , etc. have 3 rotational degrees of freedom.

Secondly, each term on right side, in above equations, is proportional to square of angular velocity and therefore, in accordance to law of equipartition, each term would contribute  $(\frac{1}{2})kT$  to the total average rotational energy.

Hence, for linear molecules the contribution is

$$\langle E_{rot} \rangle = \frac{1}{2}kT + \frac{1}{2}kT = kT \text{ per molecule}$$

And for non-linear molecules the contribution is

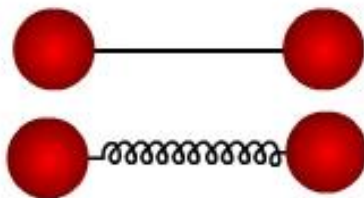
$$\langle E_{rot} \rangle = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT \text{ per molecule}$$

} (2.7)

### • Vibrational Degrees of Freedom

Vibrational motion of any molecule (Again note that Vibrational degrees of freedom do not exist for an atom) can be ascribed to normal modes of vibration. "A normal mode of vibration is defined as the molecular motion in which all the atoms in the molecule vibrate with the same frequency & all the atoms pass through their equilibrium positions simultaneously". Modes of vibration may result in the stretching & bending of molecular bonds (Just like a spring and therefore molecule exhibits simple harmonic motion)

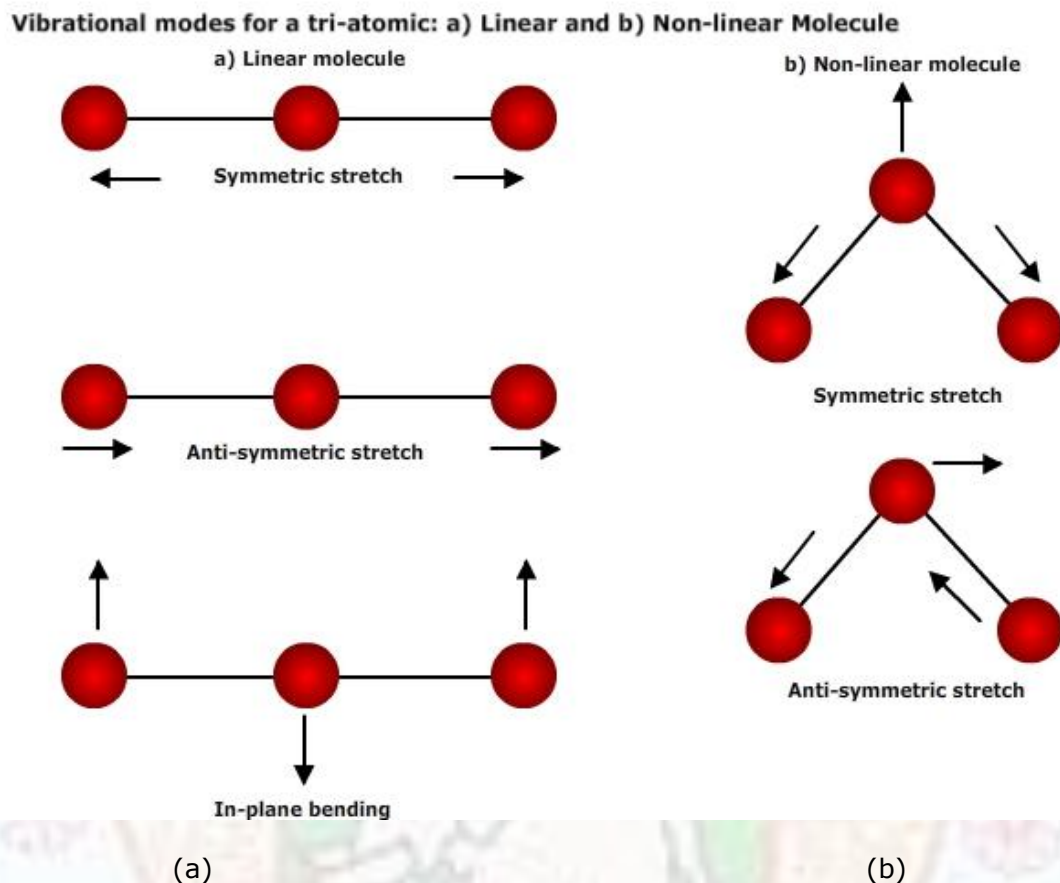
**Vibration mode for a linear diatomic molecule (e.g. Chlorine, Hydrogen)**



**Source: Author, In House ILL**

## Lesson 2: Distribution of Molecular speeds: Maxwell-Boltzmann Distribution

**Figure 2.5** Vibrational modes for a linear molecule (diatomic molecule)



Source: Author, In House ILL

**Figure 2.6** Vibrational modes (stretching and bending) for a tri-atomic molecule a) linear and b) Non-linear

Assuming these vibrations to be simple harmonic, the average energy of vibration is said to consist of two terms:

$$\langle E_{vib} \rangle = K.E + P.E$$

$$i.e. \langle E_{vib} \rangle = \frac{1}{2}\mu \left(\frac{dr}{dt}\right)^2 + \frac{1}{2}k(r - r_0)^2$$

where,  $\mu$  is the reduced mass,  $k$  is force constant,  $r_0$  is equilibrium position &  $\frac{dr}{dt}$  is the velocity.

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Now, in accordance with the law of equipartition of energy, since first term is proportional to square of velocity and second term is proportional to the square of position coordinate, hence, each term would contribute  $(\frac{1}{2})kT$  to average vibrational energy.

Therefore, each vibrational mode would contribute  $= \frac{1}{2}kT + \frac{1}{2}kT = kT$  to the average vibrational energy. Now we need to calculate possible number of vibrational modes (or degrees of freedom) for linear and non-linear molecules. So that, this number can be multiplied by  $kT$  for total vibrational contribution.

### Number of Vibrational Modes in linear molecules:

As already discussed, for a polyatomic molecule having **N** atoms, there are total of **3N** degrees of freedom. Therefore, number of vibrational degrees of freedom can be calculated by subtracting sum of rotational & translational degrees of freedom from **3N**.

**For linear molecules**, there are three translational & two rotational degrees of freedom. Hence, vibrational degrees of freedom for linear molecules are **3N-5**

Similarly, for **non-linear molecules**, there are three translational & three rotational degrees of freedom. Hence, vibrational degrees of freedom for non-linear molecules are **3N-6**

### Contribution of vibrational modes to average vibrational energy is:

For linear molecules,  $\langle E_{vib} \rangle = (3N - 5)kT$

For non-linear molecules,  $\langle E_{vib} \rangle = (3N - 6)kT$

(2.8)



### Do you know?

- **Why for linear molecules there are only two rotational degrees of freedom while for the non-linear molecules there are three degrees of freedom?**

Hint:  $E_{rot} = (\frac{1}{2})I\omega^2$  and according to the law of equipartition of energy, there will be three equal contribution in  $E_{rot}$  from the x, y and z axes.

For linear molecules, the principal axis of the molecule and x-axis are same due to which moment of inertia along this axis is zero. Thus, contribution of x-axis in the  $E_{rot}$  comes out to be zero and we only left with contribution from y and z axes.

For non-linear molecules, the principal axis of the molecule does not coincide with the three axes viz. x, y and z, and therefore, all the three axes contribute in the moment of inertia. Thus, there are three degrees of freedom in the non-linear molecule.

- **Total average energy**



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The total average energy per molecule is sum of contribution from translational, rotational & vibrational energies, i.e. using equations 2.6 to 2.8, we get

$$\langle E \rangle = \langle E_{trans} \rangle + \langle E_{rot} \rangle + \langle E_{vib} \rangle$$

$$\langle E \rangle = \frac{3}{2}kT + kT + (3N - 5)kT \text{ per molecule} \quad (\text{for linear polyatomic gases})$$

$$\langle E \rangle = \frac{3}{2}kT + \frac{3}{2}kT + (3N - 6)kT \text{ per molecule} \quad (\text{for non-linear polyatomic gases})$$

$$\langle E \rangle = \frac{3}{2}kT \text{ per molecule} \quad (\text{for monoatomic gases})$$

Multiplying by  $N_A$ , we would get total average energy per mole

$$\langle E \rangle = \frac{3}{2}RT + RT + (3N - 5)RT \text{ per mol} \quad (\text{for linear polyatomic gases})$$

$$\langle E \rangle = \frac{3}{2}RT + \frac{3}{2}RT + (3N - 6)RT \text{ per mol} \quad (\text{for non-linear polyatomic gases})$$

$$\langle E \rangle = \frac{3}{2}RT \text{ per mol} \quad (\text{for monoatomic gases})$$

(2.9)

(Note that there is no contribution from rotational and vibrational degrees of freedom for monoatomic gases.)

### 1.2.3.3 Molecular Basis of Heat Capacities

The kinetic theory of gases together with the law of equipartition of energy provides satisfactory prediction of specific heat capacities of gases.

Specific heat capacity of a substance is the amount of heat (in Joules) required to raise the temperature of one gram of the substance by 1 K. When the substance is one mole then it is called molar heat capacity.

Heat capacity is a path function so its value will differ in magnitude with a different path. Generally, heat capacity is determined by following two different paths, first at constant volume, denoted by  $C_V$  and, second at constant pressure, denoted by  $C_P$ .

Molar heat capacity at constant volume ( $C_V$ ),

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V$$

Molar heat capacity at constant pressure ( $C_P$ ),

$$C_P = \left( \frac{\partial E}{\partial T} \right)_P$$

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Therefore, if we differentiate Energy with respect to temperature, we get a predicted value of  $C_V$ . Using, equation 2.9 and differentiating it with T, we get

$$\begin{aligned} C_V &= \frac{3}{2}R + R + (3N - 5)R = \frac{5}{2}R + (3N - 5)R && \text{(for linear polyatomic gases)} \\ C_V &= \frac{3}{2}R + \frac{3}{2}R + (3N - 6)R = 3R + (3N - 6)R && \text{(for non-linear polyatomic gases)} \\ C_V &= \frac{3}{2}R && \text{(for monoatomic gases)} \end{aligned} \quad (2.10)$$


Now, molar heat capacity at constant pressure can be calculated by using the relation

$$C_p = C_V + R$$

We get,

$$\begin{aligned} C_p &= \frac{5}{2}R + (3N - 5)R + R = \frac{7}{2}R + (3N - 5)R && \text{(for linear polyatomic gases)} \\ C_p &= 3R + (3N - 6)R + R = 4R + (3N - 6)R && \text{(for non-linear polyatomic gases)} \\ C_p &= \frac{3}{2}R + R = \frac{5}{2}R && \text{(for monoatomic gases)} \end{aligned} \quad (2.11)$$

**The ratio of  $C_p/C_V$  is represented as  $\gamma$ .** This ratio can be measured using Ruchardt method<sup>12</sup>.


<b>Think about it?</b>
<p>✚ Why, during calculation of heat capacity of a gas, no contribution is considered from the electronic energy? Or Why electronic energy does not contribute in the heat capacity of a molecule?</p>
<p><b>Hint: At normal temperature, a gas does not possess electronic energy as heating a molecule has negligible effect on the electrons. Only at very high temperature, electronic energy contributes to heat capacity.</b></p>

**Point to remember:** Vibrational energy contribution to heat capacity is generally neglected at normal temperature as vibration energy gap is usually much greater than RT.

**Examples for calculating  $C_V$ ,  $C_p$  and  $\gamma$  are as follows:**

For monoatomic gases,

$$C_V = \frac{3}{2}R; C_p = \frac{5}{2}R; \therefore \gamma = \frac{5/2R}{3/2R} = \frac{5}{3} = 1.67$$

For diatomic gases,

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$$C_V = \frac{5}{2}R + (3 \times 2 - 5)R = \frac{7}{2}R = 3.5R$$

$$C_P = \frac{7}{2}R + (3 \times 2 - 5)R = \frac{9}{2}R = 4.5R$$

$$\therefore \gamma = \frac{4.5R}{3.5R} = 1.2857$$

For linear triatomic gases,

$$C_V = \frac{5}{2}R + (3 \times 3 - 5)R = \frac{13}{2}R = 6.5R$$

$$C_P = \frac{7}{2}R + (3 \times 3 - 5)R = \frac{15}{2}R = 7.5R$$

$$\therefore \gamma = \frac{7.5R}{6.5R} = 1.1538$$

For non-linear triatomic gases,

$$C_V = 3R + (3 \times 3 - 6)R = 6R$$

$$C_P = 4R + (3 \times 3 - 6)R = 7R$$

$$\therefore \gamma = \frac{7R}{6R} = 1.1667$$

Predicted Values:			
Types of gas	$C_V$	$C_P$	$\gamma$
<b>Monoatomic</b>	$(3/2) R$	$(5/2) R$	1.67
<b>Diatomic</b>	$(3.5) R$	$(4.5) R$	1.28
<b>Linear Triatomic</b>	$(6.5) R$	$(7.5) R$	1.15
<b>Non-linear Triatomic</b>	$6R$	$7R$	1.17

Comparison of predicted values with experimental values:

Comparison of predicted and experimental values of $C_V$ :		
Type of gas	$C_V$ (Predicted) (J K <sup>-1</sup> mol <sup>-1</sup> )	$C_V$ (Experimental) (J K <sup>-1</sup> mol <sup>-1</sup> )
<b>Monoatomic</b>	12.471	12.5 (He, Ne, Ar, Kr, Xe)
<b>Diatomic</b>	29.099	20.52 (H <sub>2</sub> ), 20.83 (CO), 21.54 (NO), 28.52 (I <sub>2</sub> )

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<b>Linear Triatomic</b>	54.041	28.81 (CO <sub>2</sub> ), 37.33 (CS <sub>2</sub> )
<b>Non-linear Triatomic</b>	49.884	25.26 (H <sub>2</sub> O), 25.69 (H <sub>2</sub> S), 31.51 (SO <sub>2</sub> )

The experimental value of  $C_v$  for monoatomic gases is  $12.5 \text{ J K}^{-1} \text{ mol}^{-1}$  which is in excellent agreement with the predicted one ( $1.5R = 1.5 \times 8.314 = 12.47 \text{ J K}^{-1} \text{ mol}^{-1}$ ). This value is independent of temperature over a wide range.

For polyatomic gases, it can be seen from the above table that the experimental values are lower than the predicted values and they are not independent of temperature. For diatomic gases, experimental value for  $C_v$  lies between 20.78 to 29.10 (more close to 20.78) but the predicted value is 29.10. For non-linear molecules the experimental values are very much lower than the predicted ones.

This anomaly can be attributed to the fact that law of equipartition of energy is a classical law which state that heat capacities of the gases are independent of temperature. But, later Einstein showed that heat capacities changes with the temperature i.e. it is a function of temperature. When, we take quantum mechanical aspect of energy (esp. vibrational energy) into account an exponential factor comes into picture (a function of temperature) which decrease the magnitude of  $C_v$  (details of Einstien function can be seen in Statistical mechanics).

### Summary

- ✓ The maxima in the Maxwell- Boltzmann distribution correspond to the most probable speed of the gaseous molecules.
- ✓ Heavier a gas narrower is its Maxwell- Boltzmann distribution.
- ✓  $u_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}}$ ;  $u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$ ;  $u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$
- ✓  $u_{\text{rms}} : u_{\text{avg}} : u_{\text{mp}} = 1 : 0.92 : 0.82$
- ✓ **Law of Equipartition of energy:** It states that energy is equally distributed amongst all possible degrees of freedom of a system and contribution of each degree of freedom is  $(1/2)kT$ .
- ✓ Energy contribution per degree of freedom (translational or rotational) =  $\frac{1}{2} kT$



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- ✓ Energy contribution per vibrational degree of freedom =  $kT$ .
- ✓ **The average translational kinetic energy** is equal to  $\frac{3}{2} kT$  per molecule/atom.
- ✓ **The average rotational energy:**  
 For a linear molecule =  $kT$  per molecule  
 For a non-linear molecule =  $\frac{3}{2} kT$  per molecule.
- ✓ **The number of vibrational degrees of freedom:**  
 For linear molecules =  $(3N - 5)$   
 For non-linear molecules =  $(3N - 6)$ , where  $N$  is the number of atom in the molecule.
- ✓ **The total average energy** per molecule is sum of contribution from translational, rotational & vibrational energies i.e.  $\langle E \rangle = \langle E_{trans} \rangle + \langle E_{rot} \rangle + \langle E_{vib} \rangle$

Gas type	Total average energy, $\langle E \rangle$ / molecule
Monoatomic	$\frac{3}{2}kT$
Linear polyatomic	$\frac{3}{2}kT + kT + (3N - 5)kT$
Non-linear polyatomic	$\frac{3}{2}kT + \frac{3}{2}kT + (3N - 6)kT$

- ✓  $C_V = \left(\frac{\partial E}{\partial T}\right)_V$ ;  $C_P = \left(\frac{\partial E}{\partial T}\right)_P$ ;  $C_P - C_V = R$
- ✓  $C_P/C_V = \gamma$
- ✓ Following are the relations for  $C_V$  and  $C_P$  for different types of gases:

Gas type	$C_V$	$C_P$
Monoatomic	$(3/2)R$	$(5/2)R$
Linear polyatomic	$(5/2)R + (3N - 5)R$	$(7/2)R + (3N - 5)R$
Non-linear polyatomic	$3R + (3N - 6)R$	$4R + (3N - 6)R$

## Exercise

### A. Fill in the blanks:

1. When temperature is -----, the most probable speed of the molecules increases.
2. Maxwell Boltzmann distribution for the heavier gases becomes-----.
3. The speed which most of the molecules possess at any given temperature is known as-----.



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- The magnitude of root mean square speed of gaseous molecules is always ----- than the most probable speed of the gaseous molecules.
- The number of rotational degrees of freedom for a linear molecule is ---- and that for non-linear molecule is-----.
- The total average energy of a molecule is a sum of ----- type of energies.
- The ratio of  $C_p/C_v$  is represented by-----.
- The value of  $C_v$  and  $C_p$  for a monoatomic gases are -----and -----respectively.
- In a Maxwell Distribution plot ---- is plotted on the x-axis.
- Maxima observed in the Maxwell distribution curve corresponds to ---- speed.

### B. Objective questions:

- Which of the following gaseous molecule has the highest average speed at 298 K?
  - $N_2$
  - $O_2$
  - $H_2$
  - $CO_2$
- Two molecules of a Helium gas have speed of  $3 \text{ ms}^{-1}$  and  $4 \text{ ms}^{-1}$  respectively. The root mean square speed at a particular temperature is
  - $(3+4)/2$
  - $(9+16)/2$
  - $(25/2)^{1/2}$
  - $\sqrt{25}/2$
- Which of the following order is true?
  - $u_{rms} > u_{avg} > u_{mp}$
  - $u_{avg} > u_{rms} > u_{mp}$
  - $u_{avg} > u_{mp} > u_{rms}$
  - $u_{rms} > u_{mp} > u_{avg}$
- Which of the following is the expression of root mean square speed?
  - $3RT/M$
  - $\sqrt{3RT/M}$
  - $\sqrt{M/3RT}$
  - $RT/3M$
- Among the following gases, which one will have the least magnitude of root mean square speed at 300 K?

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- a.  $\text{CO}_2$
  - b.  $\text{NO}$
  - c.  $\text{NO}_2$
  - d.  $\text{Ne}$
6. Which of the following gas molecules will have the largest molar specific heat?
- a.  $\text{He}$
  - b.  $\text{O}_2$
  - c.  $\text{CH}_4$
  - d.  $\text{C}_6\text{H}_6$
7. Two gases, A and B are in thermal equilibrium and  $u_{\text{mp}}$  of gas B is observed to be higher than that of gas A. Which of the following must be true?
- a. Gas A has a lower temperature than gas B.
  - b. The molecules in gas A are heavier than those in gas B.
  - c. Gas A is monatomic and gas B is diatomic.
  - d. Gas A is at lower pressure than gas B.
8. Which of the following relation is true?
- a.  $C_p - C_v = 1$
  - b.  $C_p - C_v = R$
  - c.  $C_p + C_v = R$
  - d.  $C_p - C_v = k$
9. The ratio of root mean square speed of  $\text{H}_2$  at 50 K and that of  $\text{O}_2$  at 400 K is
- a. 1
  - b.  $\frac{1}{2}$
  - c. 2
  - d. 4
10. The translational, rotational and vibrational degrees of freedom for a  $\text{CH}_4$  molecule has the following values, respectively
- a. 3, 3, 6
  - b. 3, 2, 7
  - c. 2, 3, 7
  - d. 3, 4, 5

### C. True- False:

1. The average kinetic energy per molecule of an ideal gas is  $1.5RT$ .

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2. Under the identical conditions of temperature, pressure and volume, the two gases having equal mass will have same  $u_{rms}$ .
3. Water molecule has the 3 translational, 3 rotational and 3 vibrational degrees of freedom, respectively.
4. The total average energy per mol for a monoatomic gas is  $(3/2)RT$ .
5. Specific heat capacity of a substance is the amount of heat required to raise the temperature of 100 gram of the substance by 1 K.
6. Molar heat capacity at constant volume for a non-linear polyatomic gas is equal to  $(3R + (3N - 6) R)$ , where N is the number of atoms in the gas and R is the universal gas constant.
7. The most probable speed of a given gas decreases with increase in temperature.
8. As the mass of an ideal gas increases, its Maxwell Boltzmann Distribution becomes broader i.e. most probable speed increases.
9. Electronic energy has no contribution in the heat capacity of an ideal gas.
10. For a benzene molecule, 30 vibrational degrees of freedom exist.

### D. Short questions and numerical

1. Illustrate the Law of Equipartition of energy with an example.
2. How the root mean square speed, average speed and most probable speed of a gas related to each other?
3. Give values of  $\gamma$  for  $CO_2$ ,  $H_2O$  and  $N_2$ .
4. Discuss the deviations observed in the predicted and experimental values of  $C_V$  for di- and triatomic gases.
5. At what temperature will  $N_2$  molecules have the same r.m.s. speed as  $O_2$  molecules at 298 K?
6. The density of nitrogen at 300 K and 2 atm is 1.43 g/L. Calculate the most probable speed of nitrogen at the same temperature.
7. Determine the mean square deviation,  $\langle(u - \langle u \rangle)^2\rangle$  for He at 298 K, where u is the speed of the He molecules.
8. The most probable speed of  $NO_2$  gas at STP is  $4.20 \times 10^4 \text{ ms}^{-1}$ . Find out its average speed and root mean square speed under similar conditions.
9. Calculate the mass of a gas A which has most probable speed equal to  $1500 \text{ ms}^{-1}$  at a temperature of 4330 K.

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10. At what temperature the root mean square speed of  $O_2$  equals to that of He at 40 K, assuming the ideal behavior of the two gases.

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