CHE 2615
Physical Chemistry

LECTURE 4: THE KINETIC MODEL OF GASES (Part B)

UNZA

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Distribution of molecular velocities

- While deriving **Kinetic Gas Equation**, it was assumed that all molecules in a gas have the same velocity.
- ***But it is not so***.
- When any two molecules collide, one molecule transfers kinetic energy ($\frac{1}{2}mv^2$) to the other molecule.
- The velocity of the molecule which gains energy increases and that of the other decreases.

Distribution of molecular velocities

- Millions of such molecular collisions are taking place per second.
- Therefore, the velocities of molecules are changing constantly.
- Since the number of molecules is very large, a fraction of molecules will have the same particular velocity.
- In this way there is a broad distribution of velocities over different fractions of molecules.

Distribution of molecular velocities

- In 1860 James Clark Maxwell calculated the distribution of velocities from the laws of probability.
- He derived the following equation for the distribution of molecular velocities.

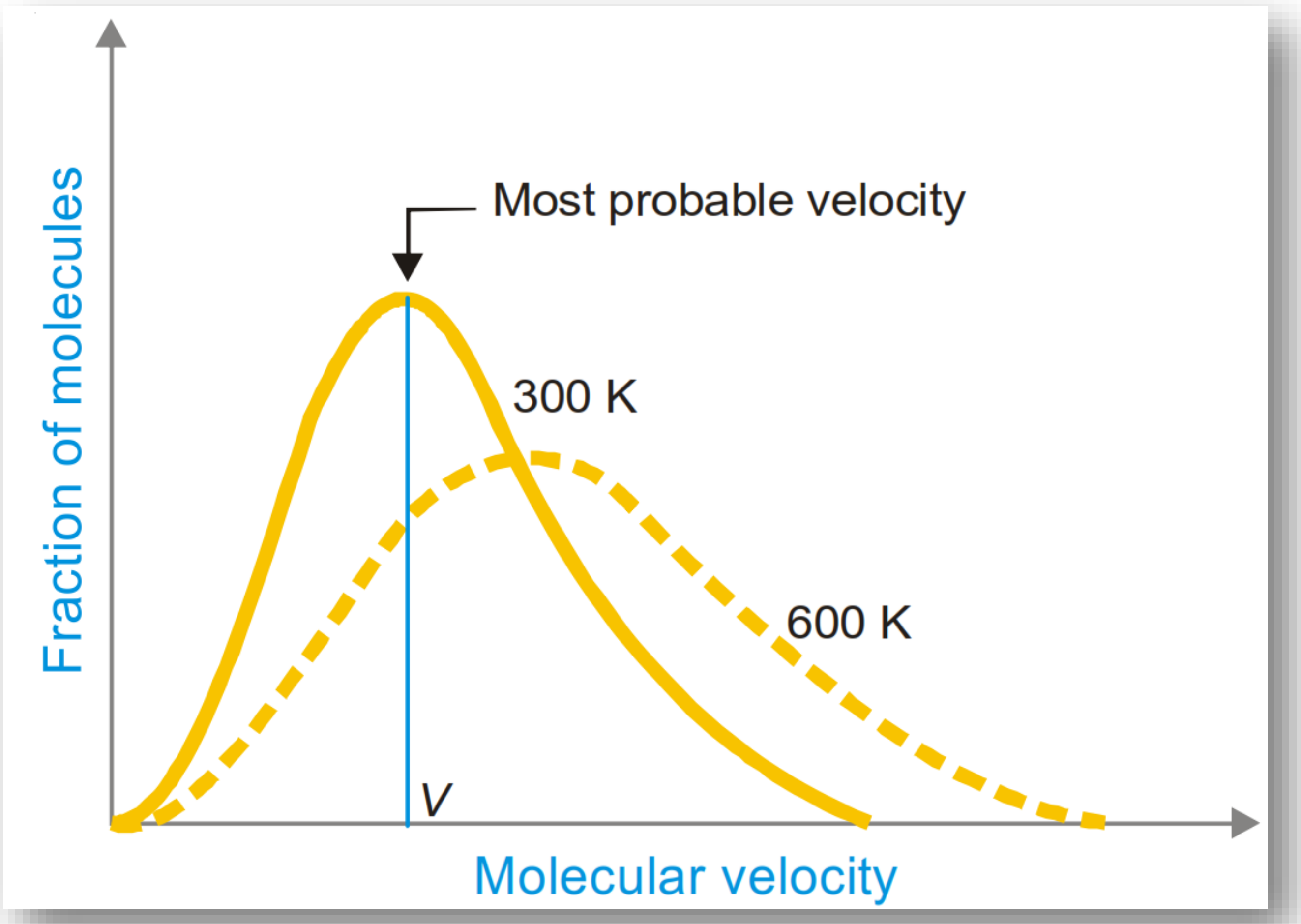
$$\frac{dN_c}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{\frac{-MC^2}{2RT}} C^2\, dc$$

Distribution of molecular velocities

- where
  - dN_c = number of molecules having velocities between *C and (C + dc)*
  - *N = total number of molecules*
  - *M = molecular mass*
  - *T = temperature on absolute scale (K)*
- The relation stated above is called **Maxwell's law of distribution of velocities.**

Distribution of molecular velocities

- The fig. shows the distribution of velocities in nitrogen gas, N_2, at 300 K and 600 K.



Distribution of molecular velocities

- It will be noticed that:
  1) A very small fraction of molecules has either very low (close to zero) or very high velocities.
  2) Most intermediate fractions of molecules have velocities close to an average velocity represented by the peak of the curve.
     - This velocity is called the **most probable velocity.**

Distribution of molecular velocities

- **It** may be defined as the velocity possessed by the largest fraction of molecules corresponding to the highest point on the Maxvellian curve.

3) At higher temperature, the whole curve shifts to the right (dotted curve at 600 K).

   - This shows that **at higher temperature more molecules have higher velocities and fewer molecules have lower velocities.**

Average Velocity

- In our study of kinetic theory we come across three different kinds of molecular velocities:
  1. the Average velocity (v_{av})
  2. the Root Mean Square velocity (u)
  3. the Most Probable velocity (v_{mps})
- **Average Velocity**
- Let there be n molecules of a gas having individual velocities v_1, v_2, v_3 ..... v_n
- The ordinary average velocity is the arithmetic mean of the various velocities of the molecules.

Average Velocity

$$\bar{v} = \frac{v_1 + v_2 + v_3 \; ..... + v_n}{n}$$

- From Maxwell equation it has been established that the average velocity v_{av} is given by the expression:

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

- Substituting the values of *R, T, π and M in this expression, the average value can be calculated.*

Root Mean Square Velocity

- If v_1, v_2, v_3 ..... v_n are the velocities of *n molecules in a gas, u^2*, the mean of the squares of all the velocities is

$$\mu^2 = \frac{v_1^2 + v_2^2 + v_3^2 \ ..... + v_n^2}{n}$$

- Taking the root

$$\mu = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 \ ..... + v_n^2}{n}}$$

- μ is thus the **Root Mean Square velocity or RMS velocity. It is denoted by *u*.**

Root Mean Square Velocity

- The value of the RMS of velocity *u*, at a given temperature can be calculated from the Kinetic Gas Equation.

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

$$u^2 = \frac{3PV}{mN}$$

- For one mole of gas

$$PV = RT$$

Root Mean Square Velocity

- Therefore,

$$u^2 = \frac{3RT}{M}$$

- Where *M* (m*N*) is the molar mass
- By substituting the values of *R, T and M, the value of u (RMS velocity) can be determined.*
- RMS velocity is superior to the average velocity considered earlier.
- With the help of *u, the **total*** **Kinetic energy** of a gas sample can be calculated.

Most Probable Velocity

- As already stated the most probable velocity is possessed by the largest number of molecules in a gas.
- According to the calculations made by Maxwell, the most probably velocity, v_{mp}, is given by:

$$v_{mps} \quad \sqrt{\frac{2RT}{M}}$$

- Substituting the values of R, T and M in this expression, the v_{mp} can be calculated.

Relation between Average Velocity, RMS Velocity and Most Probable Velocity

- We know that the average velocity, $\tilde{v}$, is given by:

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

and

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

$$\therefore \quad \frac{\bar{v}}{\mu} = \sqrt{\frac{8RT}{\pi M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{8}{3\pi}}$$

$$= 0.9213$$

$$\bar{v} = \mu \times 0.9213$$

Relation between Average Velocity, RMS Velocity and Most Probable Velocity

- The expression for the most probably velocity, v_{mp}, is

$$v_{mp} = \sqrt{\frac{2RT}{M}}$$

and

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

$$\therefore \quad \frac{v_{mp}}{\mu} = \sqrt{\frac{2RT}{M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{2}{3}} = 0.8165$$

$$v_{mp} = \mu \times 0.8165$$