Ministry of Higher Education
and Scientific Research

Al-Muthanna University

College of Science

Department of Chemistry

وزارة الــتعليم الــعالــي والــبحث الــعلمي

جـــامعـــــــة الــمثنــــــــــى

كليــــة الــعلـــــــــــوم

قســــــــم الــكــيمــياء

Physical Chemistry

المحـــاضـرة 4

المرحلـة الثانــية

أ.د. حـــســن صبـيح جـبر

جـــــــامـــعة المثنــــــى

كلـــــــية العلـــــــوم

قســـــــــم الكيميــــــاء

الكيمياء الفيزيائية - الكورس الاول

ا.د. حســـن صبيــح

Distribution of molecular speeds

In a real gas sample at a given temperature T, all molecules do not travel at the same speed. Some move more rapidly than others.

• In a real gas the speeds of individual molecules span wide ranges with constant collisions continually changing the molecular speeds.

• Maxwell and independently Boltzmann analysed the molecular speed distribution in an ideal gas, and derived a mathematical expression for the speed distribution f(v).

• This formula enables one to calculate various statistically relevant quantities such as the average velocity of a gas sample, the rms velocity, and the most probable velocity of a molecule in a gas sample at a given temperature T.

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$$F(v) = 4\pi v^2 \left\{ \frac{m}{2\pi k_B T} \right\}^{3/2} \exp\left[-\frac{mv^2}{2k_B T} \right] \qquad (1.15)$$

In Figure 1.6, **the peak of the most probable spee**d increases as temperature increases. Also, it flattens out increasing with increasing temperature.

In Figure 1.7 light molecules have high **average speed** and a wide spread of speeds.

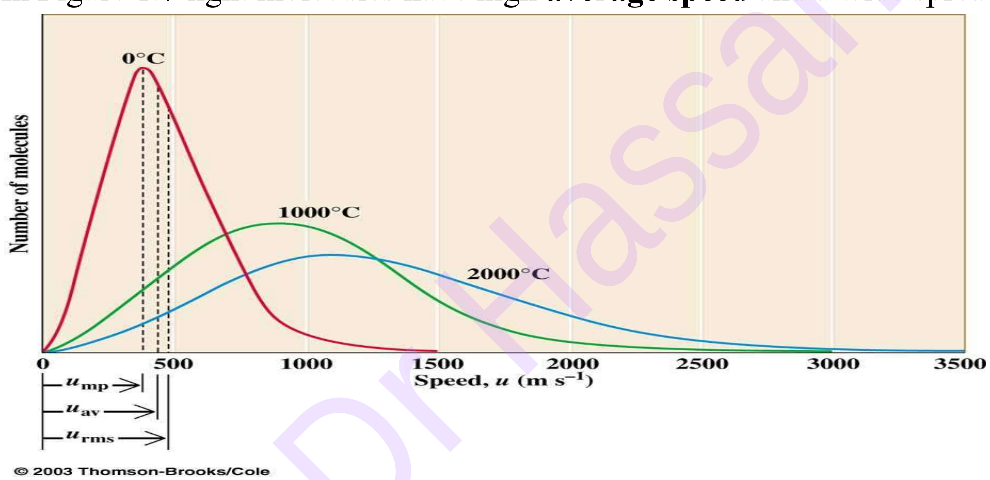


Figure 1.6 Maxwell-Boltzmann distributions of molecular speeds at three temperatures.

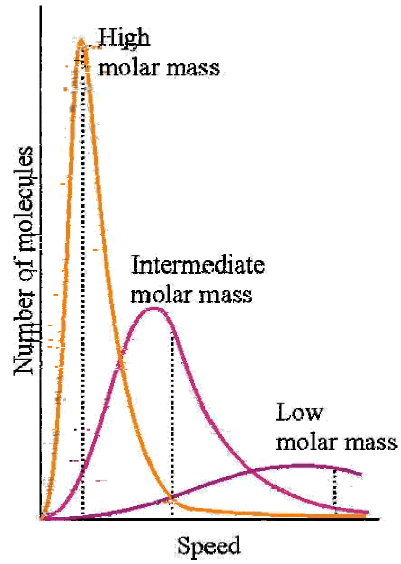


Figure 1.7 Maxwell-Boltzmann distribution of molecular speeds at three molar masses.

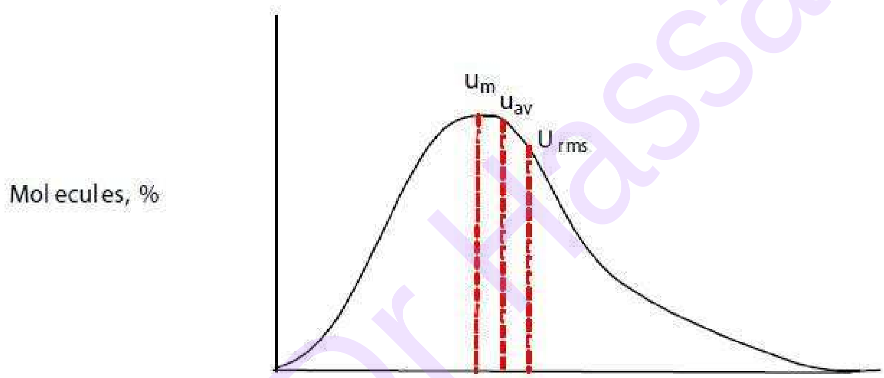
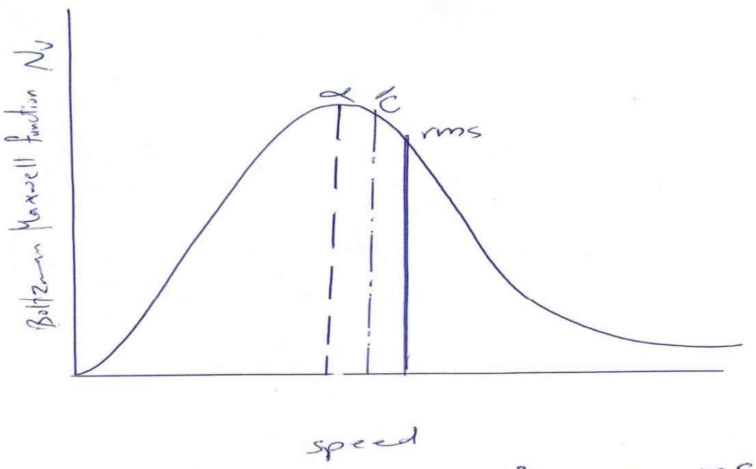


Figure 1.8 Diagram showing the different characteristics speeds for a sample of gas Molecules, %

$$u_{avg} = \sqrt{\frac{8RT}{\pi M}}$$

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



where $N_v = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} \bar{C}^2 e^{-mC_2/2k_BT}$

m = mass , KB Boltzman constant , T = temp.

$$\alpha : \bar{C} : rms$$

$$\left(\frac{2RT}{M}\right)^{1/2} : \left(\frac{8RT}{\pi M}\right)^{1/2} : \left(\frac{3RT}{M}\right)^{1/2}$$

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

$$0.82 : 0.92 : 1.00$$

Three characteristic speeds are shown in the diagram. More molecules have the speed u_m, known as the most probable or modal speed, than the other two. The simple average speed is u_{av} whilst u_{rms} is the square root of the average of the squares of speeds of all molecules in a sample.

<u>Diffusion and effusion of gases</u>

Diffusion is the migration of molecules of different substances as a result of the random motion of molecules. Although gas molecules are consistently having collisions resulting in frequent changes in direction, the net rate at which a gas moves in a particular direction depends on the average speed. Diffusion always proceeds from a region of higher concentration to one of lower concentration.

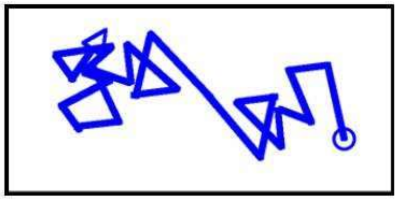


Figure 1.9 Path travelled by a single gas molecule in which each change in direction represents a collision.

Effusion is a process related to diffusion, it is the escape of gas molecules from their container through an orifice (pinhole). Consider the effusion of a mixture of gases through an orifice as shown in the figure below.

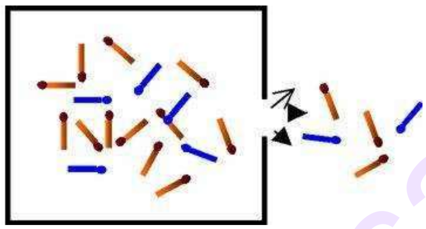


Figure 1.10 Path travelled by a single gas molecule in which each change in direction represents a collision.

$$\frac{\text{Rate effusion of A}}{\text{Rate effusion of B}} = \frac{u_{rms}\,(\text{A})}{u_{rms}\,(\text{B})} = \sqrt{\frac{3RT\,/\,M_A}{3RT\,/\,M_B}} \qquad (1.16)$$

This result is a statement of Graham‟s law, which states that the rate of effusion (or diffusion) of two different gases are inversely proportional to the square roots of their molar masses.
In considering the equation above it is evident that lighter gases will effuse faster than the heavier gases. The consequences of the above theory maybe summarised that ratios of the root-mean-square speeds are equal to the ratios of

- rates of effusion
- effusion times
- amount of gas effused
- distance travelled by the molecules

- amount of gas effused
- molecular speeds

Example 1.9

Calculate the ratio of the diffusion rate for H_2O and D_2O (D is deuterium an isotope of hydrogen).

Molar mass H_2O = 18.01 g mol $^{-1}$, D_2O = 19.01 g mol $^{-1}$

$$\frac{\text{Rate diffusion } H_2O}{\text{Rate diffusion } D_2O} = \sqrt{\frac{M_{H_2O}}{M_{D_2O}}} = \sqrt{\frac{19.01 \text{ g mol}^{-1}}{18.01 \text{ g mol}^{-1}}} = 1.02$$

Practice problem 1.6

Two gases, HBr and CH_4, effuse through a small opening. HBr effuses through the opening at a rate of 4 cm^3 s^{-1}, at what rate will the CH_4 molecules effuse through the same opening.

(a) 9 cm^3 s^{-1} (b) 10 cm^3 s^{-1} (c) 8.5 cm^3 s^{-1} (d) 9 m^3 s^{-1}

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