

Ministry of Higher Education
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وزارة التعليم العالي والبحث
العلمي

جامعة المثنى

كلية العلوم

قسم الكيمياء

Physical Chemistry

المحاضرة 3

المرحلة الثانية

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Kinetic molecular theory of gases

Chiefly Rudolf Clausius (1822-1906), James Clerk Maxwell (1831-1879) and Ludwig Boltzmann (1844-1888) developed the kinetic molecular theory. Their theory is based on the following assumptions about the nature of gases at molecular level.

1. Molecules in a gas are in constant random motion and frequently collide with each other.
2. A gas consists of a large number of particles that are so small and separated by such large distances that their size is negligible. Attractive and repulsive forces between gas molecules are negligible.
3. Each molecule acts independent of the other molecules and is unaffected by their presence. At sufficiently low temperatures, all gases will condense into liquids suggesting the presence of intermolecular forces that become significant at low temperatures. Attractive forces are responsible for holding liquid and solid molecules together. The tendency for a gas to expand and fill the volume in which it occupies suggests the presence of negligible forces of attraction between molecules. Increasing pressure of a gas results in decrease of inter- particle distance and therefore more interaction between molecules.

Molecules collide with each other and the walls of the container. In these collisions, individual molecules may gain or lose energy. However, in a collection of molecules at constant temperature the total energy remains constant. The assumption is valid in the sense that if it were not true, then the pressure of a gas would decrease gradually as it is a consequence of collisions with the wall of the container.

5. The average kinetic energy of the molecules which is proportional to the temperature of the gas in Kelvin. Any two gases at the same temperature will have the same average kinetic energy.

Gas pressure derived from KMT analysis (Kinetic Equation of Gases)

The pressure of a gas can be explained by KMT as arising from the force exerted by gas molecules impacting on the walls of a container (assumed to be a cube of side length L

and hence of Volume L^3 . In addition, area of each side is L^2 and the total area is $6 L^2$. We consider a gas of N molecules each of mass m contained in cube of volume $V = L^3$.

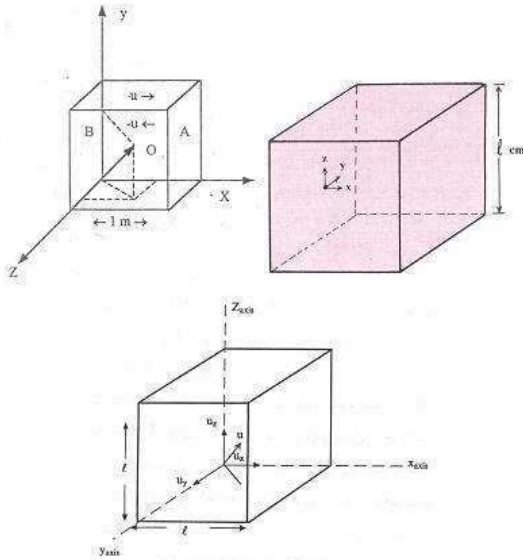


Figure 1.5 A gas container (assumed to be a cube of side length L and hence of Volume L^3).

When gas molecule collides (with speed v_x) with wall of the container perpendicular to x co-ordinate axis and bounces off in the opposite direction with the same speed (an elastic collision) then the momentum lost by the particle and gained by the wall is Δp_x
 $\Delta p_x = mv_x - (-mv_x) = 2mv_x$

The particle impacts the wall once every $2L/v_x$ time units

$$\Delta t = \frac{2L}{v_x}$$

The number of collisions in 1 second is $2L / v_x$ collisions.

The force F due to the particle can then be computed as the rate of change of momentum with respect to time (Newton Second Law).

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{l}$$

The force of the two sides along X -axis is

$$F = 2 \frac{m}{L} v_x^2$$

The magnitude of the velocity v of any particle j can also be calculated from the relevant velocity components v_x , v_y , and v_z .

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

Force acting on the six walls is

$$F = 2 \frac{m}{L} (v^2 = v_x^2 + v_y^2 + v_z^2) = 2 \frac{m}{L} v^2$$

Force acting on the six walls from all N molecules can be computed by summing forces arising from each individual molecule j.

$$F = 2 \frac{m}{L} (v^2 = v_x^2 + v_y^2 + v_z^2) = 2 \frac{m}{L} \sum_{i=1}^N v_i^2$$

Assuming that a large number of particles are moving randomly then the force on each of the walls will be approximately the same.

$$\langle v^2 \rangle = v_{rms}^2 = \frac{1}{N} \sum_{j=1}^N v_j^2$$

Then :

$$F = 2 \frac{m}{L} N v_{rms}^2$$

The force can also be expressed in terms of the average velocity v_{rms}^2 where v_{rms} denotes the root mean square velocity of the collection of particles.

The pressure can be readily determined once the force is known using the definition $P = F/A$ where $A=6L^2$ denotes the area of the wall over which the force is exerted.

$$P = \frac{F}{A} = \frac{2 N m v_{rms}^2}{L \cdot 6L^2} = \frac{1 N m v_{rms}^2}{3 V}$$

$$PV = \frac{1}{3} N m v_{rms}^2 \quad (1.11)$$

Internal energy of an ideal gas

We have Average kinetic Energy of gas molecule is given by

$$\langle KE \rangle = \frac{1}{2} m v_{rms}^2 \quad (1.12)$$

Then

$$PV = \frac{1}{3} N m v_{rms}^2 = \frac{2}{3} \frac{1}{2} N m v_{rms}^2 = \frac{2}{3} N \left(\frac{1}{2} m v_{rms}^2 \right) = \frac{2}{3} N \langle KE \rangle$$

$$nRT = \frac{2}{3} N \langle KE \rangle$$

$$\langle KE \rangle = \frac{3 nRT}{2 N}$$

For N molecules

$$KE = N \langle KE \rangle = \frac{3}{2} nRT \quad (1.13)$$

$$\frac{P V}{n} = R T = \frac{2}{3} (K E)_{ave}$$

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$$(K E)_{ave} = \frac{3}{2} R T$$

Root-mean-square speed

We can derive a useful equation for u_{rms} . One of the results of the kinetic theory of gases is that the average kinetic energy of a gas is We have $n=N/N_A$ and $m=M/ N_A$ where M is the total mass of one mole of molecules and N_A is Avogadro's number. M_w is the molecular weight or mass of one mole.

$$KE = N \langle KE \rangle = \frac{1}{2} N m v_{rms}^2 = \frac{1}{2} n N_A m v_{rms}^2 = \frac{1}{2} n M_w v_{rms}^2 = \frac{3}{2} n R T$$
$$M_w v_{rms}^2 = 3 R T$$

$$v_{rms} = \sqrt{\frac{3RT}{M_w}} \quad (1.14)$$

Example 1.8

Calculate the root-mean-square speed in meters per second for $Cl_2(g)$ molecules at $30^\circ C$.

Solution

The expression for u_{rms} is used

$$v_{rms} = \sqrt{\frac{3RT}{M_w}}$$

For chlorine $M_w = 70.91 \text{ g} = 7.09 \times 10^{-2} \text{ kg mol}^{-1}$, $T = 303 \text{ K}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Substituting in the equation

$$v_{rms} = \sqrt{\frac{3 \times 8.314 \times 303}{7.09 \times 10^{-2}}}$$
$$= 326 \text{ m s}^{-1}$$

Practice problem 1.4

At what temperature would the u_{rms} for $Ne(g)$ be expected to be the same as that for $He(g)$ at 300 K ?

- (a) 1000 (b) 150 (c) 1500 (d) 1600
