

## 2.4: Kinetic Energy

Using expressions for  $v_{mp}$ ,  $v_{ave}$ , or  $v_{rms}$ , it is fairly simple to derive expressions for kinetic energy from the expression

$$E_{kin} = \frac{1}{2}mv^2$$

It is important to remember that there will be a full distribution of molecular speeds in a thermalized sample of gas. Some molecules will be traveling faster and some more slowly. It is also important to recognize that the most probable, average, and RMS kinetic energy terms that can be derived from the Kinetic Molecular Theory do not depend on the mass of the molecules (Table 2.4.1). As such, it can be concluded that the average kinetic energy of the molecules in a thermalized sample of gas depends only on the temperature. However, the average speed depends on the molecular mass. So, for a given temperature, light molecules will travel faster on average than heavier molecules.

Table 2.4.1: Kinetic Properties of a Thermalized Ensemble (i.e., follows Maxwell-Boltzmann Distribution)

Property	Speed	Kinetic Energy
Most probable	$\sqrt{\frac{2k_B T}{m}}$	$k_B T$
Average	$\sqrt{\frac{8k_B T}{\pi m}}$	$\frac{4k_B T}{\pi}$
Root-mean-square	$\sqrt{\frac{3k_B T}{m}}$	$\frac{3}{2}k_B T$

### The Ideal Gas Law

The expression for the root-mean-square molecular speed can be used to show that the Kinetic Molecular model of gases is consistent with the ideal gas law. Consider the expression for pressure

$$p = \frac{N_{tot}m}{3V}\langle v \rangle^2$$

Replacing  $\langle v \rangle^2$  with the square of the RMS speed expression yields

$$p = \frac{N_{tot}m}{3V} \left( \frac{3k_B T}{m} \right)$$

which simplifies to

$$p = \frac{N_{tot}k_B T}{V}$$

Noting that  $N_{tot} = n \cdot N_A$ , where  $n$  is the number of moles and  $N_A$  is Avogadro's number

$$p = \frac{nN_A k_B T}{V}$$

or

$$pV = nN_A k_B T$$

Finally, noting that  $N_A \cdot k_B = R$

$$pV = nRT$$

That's kind of cool, no? The only assumptions (beyond the postulates of the Kinetic Molecular Theory) is that the distribution of velocities for a thermalized sample of gas is described by the Maxwell-Boltzmann distribution law. The next development will be to use the Kinetic Molecular Theory to describe molecular collisions (which are essential events in many chemical reactions.)

## Collisions with the Wall

In the derivation of an expression for the pressure of a gas, it is useful to consider the frequency with which gas molecules collide with the walls of the container. To derive this expression, consider the expression for the “collision volume”.

$$V_{col} = v_x \Delta t \cdot A$$

All of the molecules within this volume, and with a velocity such that the x-component exceeds  $v_x$  (and is positive) will collide with the wall. That fraction of molecules is given by

$$N_{col} = \frac{N}{V} \frac{\langle v \rangle \Delta t \cdot A}{2}$$

and the frequency of collisions with the wall per unit area per unit time is given by

$$Z_w = \frac{N}{V} \frac{\langle v \rangle}{2}$$

In order to expand this model into a more useful form, one must consider motion in all three dimensions. Considering that

$$\langle v \rangle = \sqrt{\langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2}$$

and that

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle$$

it can be shown that

$$\langle v \rangle = 2\langle v_x \rangle$$

or

$$\langle v_x \rangle = \frac{1}{2}\langle v \rangle$$

and so

$$Z_w = \frac{1}{4} \frac{N}{V} \langle v \rangle$$

The factor of  $N/V$  is often referred to as the “number density” as it gives the number of molecules per unit volume. At 1 atm pressure and 298 K, the number density for an ideal gas is approximately  $2.5 \times 10^{19}$  molecule/cm<sup>3</sup>. (This value is easily calculated using the ideal gas law.) By comparison, the average number density for the universe is approximately 1 molecule/cm<sup>3</sup>.

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