Microscopic Properties of Gases

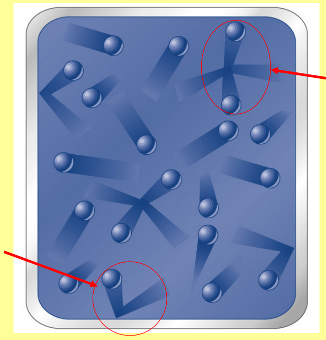
- So far we have seen the gas laws.
- These came from observations.
- In this section we want to look at a theory that explains the gas laws:

The kinetic theory of gases

or The kinetic molecular theory

Kinetic Theory of Gases: Assumptions

1. A gas is made up of a large number of extremely small particles (molecules or atoms) in constant, random, straight line motion
2. Molecules occupy very little volume (most of the container is free space)
3. Molecules collide with one another and with the walls of the container
4. There are no forces between the molecules
5. Molecules can gain or lose energy on collision but the total energy remains constant



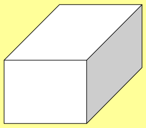
Collision between molecules

Collision with wall

The theory will give information on the speeds of molecules, the frequency with which they collide, and the distribution of energy

It is only useful if it can predict the gas laws

Pressure comes from the gas molecules hitting the walls of the container. Hence if we can determine the force with which the molecules hit the wall we can determine the pressure.



Suppose you have a gas with N identical molecules of mass m in a container of volume V.

Also assume that each molecule has a speed u, but that it can be different for different molecules.

By calculating the force that a molecule exerts on the wall, the number of collisions and averaging the result over the different molecular speeds, one gets:

$$\boxed{P = \frac{1}{3}\frac{Nm\overline{u^2}}{V}}$$

where $\overline{u^2}$ = the average of the squares of the speeds.

$$P = \frac{1}{3}\frac{Nm\overline{u^2}}{V} \qquad \therefore\ PV = \frac{1}{3}Nm\overline{u^2}$$

This is looking a lot like PV = constant

If $\overline{u^2}$ is a constant at constant temperature.

This is Boyle's Law

We will not prove this but assume it is true and use the PV equations from the macroscopic and microscopic sections to learn about speed and temperature

Temperature/kinetic energy/speed

The kinetic energy of a molecule is:

$$\tfrac{1}{2}mu^2$$

The average kinetic energy of a molecule is:

$$\frac{1}{2}m\overline{u^2}$$

The kinetic energy of a mole of molecules is

$$\frac{1}{2}N_A m\overline{u^2} \qquad (N_A \text{ is Avogadro's number})$$

The kinetic energy of a mole of molecules (E) is

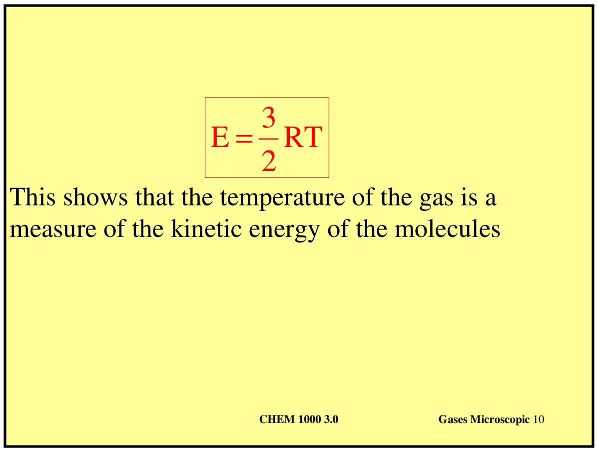
$$E = \frac{1}{2}N_A m\overline{u^2} \quad \therefore \quad m\overline{u^2} = \frac{2E}{N_A}$$

But

$$PV = \frac{1}{3}Nm\overline{u^2} = \frac{2}{3}\frac{N.E}{N_A} = \frac{2}{3}n.E$$

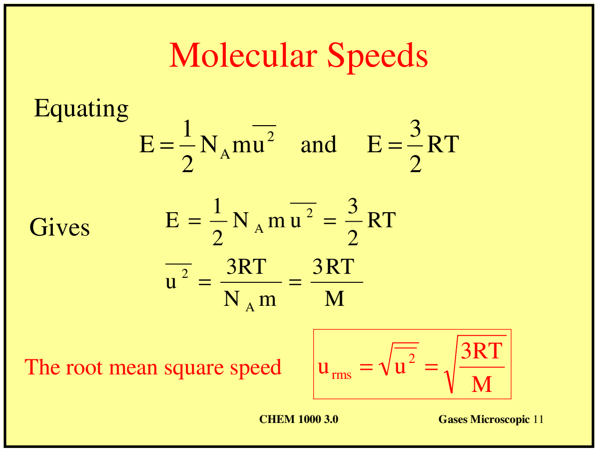
given that $PV = nRT$

$$nRT = \frac{2}{3}n.E \quad \therefore\ E = \frac{3}{2}RT$$



$$\boxed{E = \frac{3}{2}RT}$$

This shows that the temperature of the gas is a measure of the kinetic energy of the molecules



Molecular Speeds

Equating

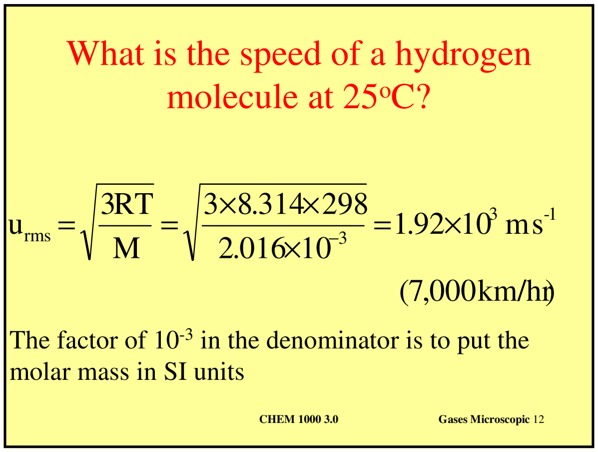
$$E = \frac{1}{2}N_A m\overline{u^2} \quad \text{and} \quad E = \frac{3}{2}RT$$

Gives

$$E = \frac{1}{2}N_A m\overline{u^2} = \frac{3}{2}RT$$

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

The root mean square speed $\boxed{u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}}$



What is the speed of a hydrogen molecule at 25°C?

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 298}{2.016 \times 10^{-3}}} = 1.92 \times 10^{3}\ \mathrm{m\,s^{-1}}$$

(7,000km/hr)

The factor of 10^{-3} in the denominator is to put the molar mass in SI units

Distribution of molecular speeds

So far we have calculated the root mean square speed only

What other speeds are possible?

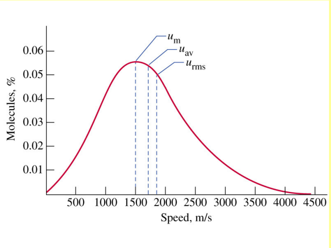
What is the real average speed?

Distribution of molecular speeds

u_m is the "most probable speed" (mode)

u_{av} is the average speed (mean)

u_{rms} is the root mean square speed



All speeds are possible but are not equally likely

Average speeds

There are three average speeds. Since the speed distribution is not symmetric, they are different

$$u_m = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2kT}{m}}$$

$$u_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}$$

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}}$$

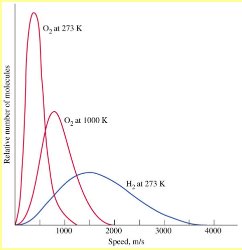
$u_m : u_{av} : u_{rms}$

$0.82 : 0.92 : 1$

Variation in speed with temperature

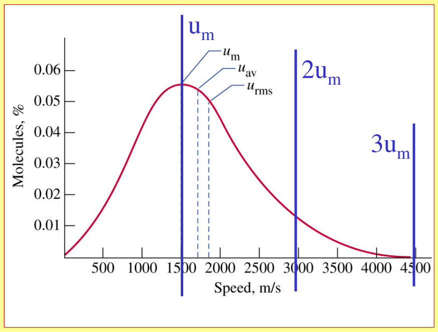
We already know that the average speeds vary with $\sqrt{T}$

The red curves are for O_2 at two temperatures.



How broad is the speed distribution

We know the average speeds. Do most molecules have speeds similar to the average? Do a lot go faster?



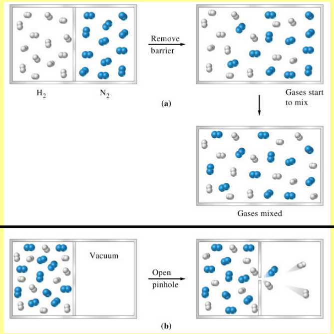
Clearly the distribution is narrow

It is possible to calculate the fraction of molecules that have a speed greater than u

Speed u	Fraction of molecules with speeds greater than u
0	1 (all molecules go faster than 0)
$3u_m$	$4.5x10^{-4}$
$5u_m$	$4x10^{-10}$
$10u_m$	$4x10^{-43}$

Most molecules have speeds close to u_m

Diffusion and Effusion



Diffusion

Effusion

Collisions with the Wall

The number of collisions that molecules make with the wall depend on how many molecules there are (per unit volume) and how fast they are moving. Z_{wall} will have units of $m^{-2}\ s^{-1}$

$$Z_{wall} \propto \frac{N}{V}.u_{av} \quad \text{actually} \quad Z_{wall} = \frac{1}{4}\frac{N}{V}.u_{av}$$

Effusion

We can obtain a quantitative understanding of effusion by recognizing that effusion is the loss of a molecule that would normally hit the wall.

$$Z_{\text{wall}} = \frac{1}{4}\frac{N}{V}.u_{\text{av}}$$

The rate at which molecules leave the container is the wall collision rate times the area of the hole

$$\text{Rate of effusion} = Z_{\text{wall}}.A = \frac{1}{4}\frac{N}{V}.u_{\text{av}}.A$$

$\therefore$ for 2 gases (A and B) in the same container

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{Z_{\text{wall}}(A).A}{Z_{\text{wall}}(B).A} = \frac{\frac{1}{4}\frac{N_A}{V}.u(A)_{\text{av}}.A}{\frac{1}{4}\frac{N_B}{V}.u(B)_{\text{av}}.A}$$

$$= \frac{N_A}{N_B}\frac{u(A)_{\text{av}}}{u(B)_{\text{av}}} = \frac{N_A}{N_B}\frac{\sqrt{8RT/\pi M_A}}{\sqrt{8RT/\pi M_B}} = \frac{N_A}{N_B}\frac{\sqrt{M_B}}{\sqrt{M_A}}$$

Note that the ratio of the number of molecules is the ratio of the partial pressures

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{P_A}{P_B}\frac{\sqrt{M_B}}{\sqrt{M_A}}$$

and for EQUAL pressures

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\sqrt{M_B}}{\sqrt{M_A}} \qquad \text{Graham's Law}$$

Aside

Students often have problems with problems involving rates and or time, because they are inverses

Always remember that $\text{Rate} = \dfrac{\text{molecules}}{\text{time}}$

So the faster the rate the smaller the time

Collisions between molecules

When studying interactions between gas molecules you need to know how often the molecules actually collide

The collision frequency is the number of collisions a particular molecule makes in one second. This will depend on how many molecules there are (per unit volume), how fast they are moving, and how big they are.

Collisions between molecules

For a gas where all the molecules are the same, and have a diameter d, the collision frequency is Z_A

$$Z_A = \sqrt{2}\pi d^2 u_{av}\frac{N}{V} = \sqrt{2}\pi d^2 u_{av}\frac{P}{kT}$$

Z_A will have units of s^{-1}

Collisions between molecules

To calculate the total number of collisions for all molecules we must multiply Z_A by N/V to count all the molecules, and by ½ so we don't count them twice.

$$Z_{AA} = \frac{1}{2}\frac{N}{V}\sqrt{2}\pi d^2 u_{av}\frac{N}{V} = \frac{1}{\sqrt{2}}\pi d^2 u_{av}\left(\frac{N}{V}\right)^2$$

Z_{AA} will have units of $s^{-1}m^{-3}$

Mean free path

A related parameter is the average distance a molecule travels between collisions. This is the mean free path

The collision frequency is Z_A s^{-1}

The time between collisions is $1/Z_A$ s

The average speed of the molecules is u_{av}

Since distance is speed times time

$$\lambda = \frac{u_{av}}{Z_A} = \frac{1}{\sqrt{2}\pi d^2}\frac{V}{N}$$

So how big are these numbers??

Nitrogen at 298K

$$u_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8\times 8.314\times 298}{\pi\times 28.01\times 10^{-3}}} = 475\ \mathrm{m\ s^{-1}} \qquad d \approx 4.0\times 10^{-10}\ \mathrm{m}$$

$$\frac{N}{V} = \frac{P}{kT} = \frac{1.013\times 10^{5}}{1.38\times 10^{-23}\times 298} = 2.46\times 10^{25}\ \mathrm{m^{-3}}$$

$$Z_{wall} = \frac{1}{4}u_{av}\frac{N}{V} = \frac{1}{4}\times 475\times 2.46\times 10^{25} = 2.92\times 10^{27}\ \mathrm{m^{-2}s^{-1}}$$

$$Z_A = \sqrt{2}\pi d^2 u_{av}\frac{N}{V} = \sqrt{2}\times\pi\times\left(4.0\times 10^{-10}\right)^2\times 475\times 2.46\times 10^{25} = 8.3\times 10^{9}\ \mathrm{s^{-1}}$$

$$\lambda = \frac{u_{av}}{Z_A} = \frac{475}{8.3\times 10^{9}} = 5.6\times 10^{-8} = 56\ \mathrm{nm}$$