Section 1: Kinetic Theory of Gases (Chapter 20.1 – 20.4)

- In this course we will learn about how molecules interact, react, and absorb/release energy.
- To react, molecules must undergo translational diffusion;
  i.e. they must have kinetic energy
- If we can develop a simple model to describe how a population of molecules diffuses we can identify factors that control collision rates, and therefore reaction rates.
- One of the simplest models is known as the kinetic theory of gases.

Three assumptions behind the kinetic theory of gases:

1. The gas consists of molecules of mass *m* in ceaseless random motion

2. The size of the molecules is negligible
i.e. diameter of molecule is much smaller than the average distance travelled between collisions

3. The molecules interact only through brief, infrequent, and elastic collisions

Actually, there is a 0^{th} assumption as well:

0. The only contribution to the energy of the gas is from the kinetic energy of the molecules.

Relationship between pressure and molecular speeds

From the 3 assumptions on the previous page it can be shown that (Justification 20.1):

$$pV = \frac{1}{3}nMc^2$$

where:
p is the pressure
V is the volume
n is the number of moles of gas
M is the molar mass of the molecules
c is the root-mean-square speed of the molecules

What is the significance of this equation?

More on root-mean-square speed *c*:

$$c = \left\langle v^2 \right\rangle^{1/2}$$

Where v is the speed of the molecules and the angular brackets denote the mean.

Test your understanding: Calculate i) the mean speed, and; ii) the root-mean-square speed, for a collection of molecules with the following speeds; 340, 333, 230, 560, 450, 326, 560, 432, 652 and 203 m s^{-1}.

A more convenient equation for *c* can be formulated via the ideal gas equation:

What can you conclude from this equation?

Test your understanding:

Which molecule will have a faster root-mean-square speed in a gas at 298K, 1 bar; CO_2 or O_2?

Will He gas at 298 K have a higher or lower root-mean-square speed than at 273 K?

What is the root-mean-square speed of nitrogen gas at 100 K?

The Maxwell distribution of speeds.

James Clerk Maxwell

1831-1879

- Maxwell recognized that molecules do not travel with a single uniform speed.
- Collisions with other molecules will alter the speeds of the individual molecules, resulting in a *distribution* of speeds.
- Maxwell derived a function $f(v)$ to describe the relative numbers of molecules travelling at a given speed, v.
- $f(v)$ is known as the Maxwell distribution of speeds

How Maxwell derived this equation:

The total kinetic energy for a molecule with velocity components v_x, v_y, and v_z is:

This energy can be related to the population of molecules with speed v ($f(v)$) by using the Boltzmann distribution (1st-year chemistry and also to be discussed later in the course):

$$f(v) = ke^{-\frac{E}{kT}}$$

We will focus on the distribution of speeds along the x-axis, since the expressions for v_y and v_z will have the same form:

$$f(v_x) = K^{1/3} e^{-mv_x^2/2kT}$$

To determine the constant K, we must normalize the distribution. The value of v_x, for example, must lie between –∞ and ∞:

$$\int_{-\infty}^{\infty} f(v_x)dv_x = 1$$

Look up the appropriate integral in a table:

$$\int_{0}^{\infty} e^{-a^2x^2}dx = \frac{\sqrt{\pi}}{2a} \quad ; a > 0$$

And we get:

$$1 = K^{1/3}\sqrt{\frac{2\pi kT}{m}}$$

and therefore

$$K = \left(\frac{m}{2\pi kT}\right)^{3/2} = \left(\frac{M}{2\pi RT}\right)^{3/2}$$

We can now write:

$$f(v_x) = \sqrt{\frac{M}{2\pi RT}}e^{-Mv_x^2/2RT}$$

Concept check: What does this equation represent?

<u>Note on units:</u>

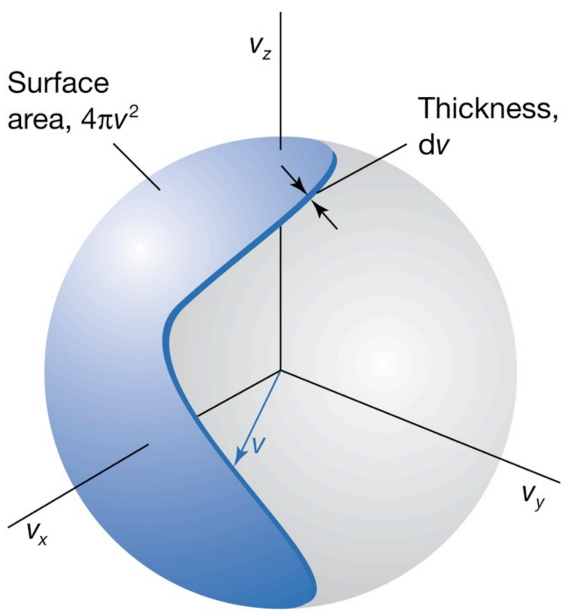
- Molar mass, M, appears in equations with the gas constant R
- mass, m, appears in equations with the Boltzmann constant, k

Putting the Maxwell Distribution Function in terms of *v*

The probability that a molecule has a velocity in the range v_x to $v_x + dv_x$, v_y to $v_y + dv_y$, v_z to $v_z + dv_z$ is:

$$f(v_x)f(v_y)f(v_z)dv_x dv_y dv_z = \left(\frac{M}{2\pi RT}\right)^{3/2} \exp\left(\frac{-Mv^2}{2RT}\right) dv_x dv_y dv_z$$

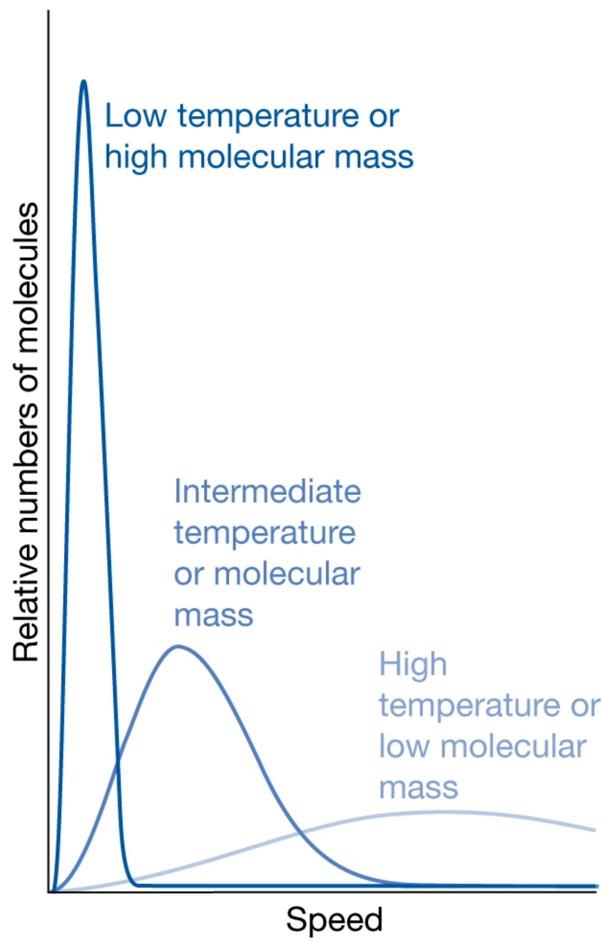
- In this equation the velocity is a vector that is defined with respect to Cartesian coordinates (v_x, v_y, v_z).
- But we do not need to know the direction that the molecule is traveling in, just its speed
  - i.e. the magnitude of the speed vector (v)
  - v does not depend on the direction in which the molecule is traveling
- We need to know the probability that the molecules have a speed in the range v to $v + dv$
- This probability is given by $4\pi v^2\, dv$ ($4\pi v^2$ is the surface area of a sphere of radius v)



The Maxwell distribution function equation:

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \exp\left(-Mv^2/2RT\right)$$

Plot of the Maxwell Distribution



True or False?

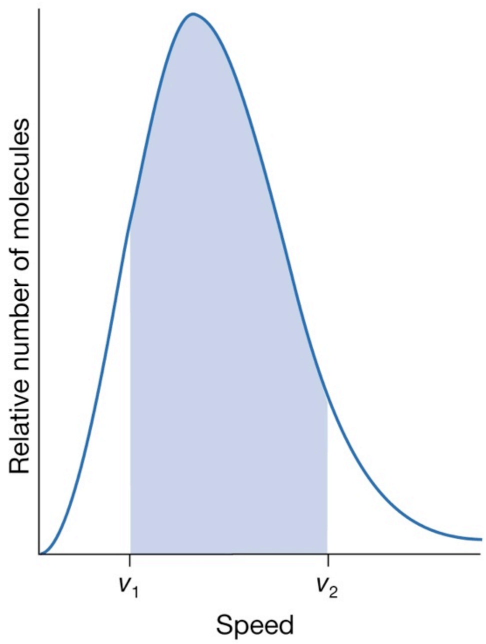
The range of speeds in a population of gas molecules increases with increasing temperatures.

The Maxwell distribution function for nitrogen gas will be the same as that for carbon dioxide gas under the same conditions.

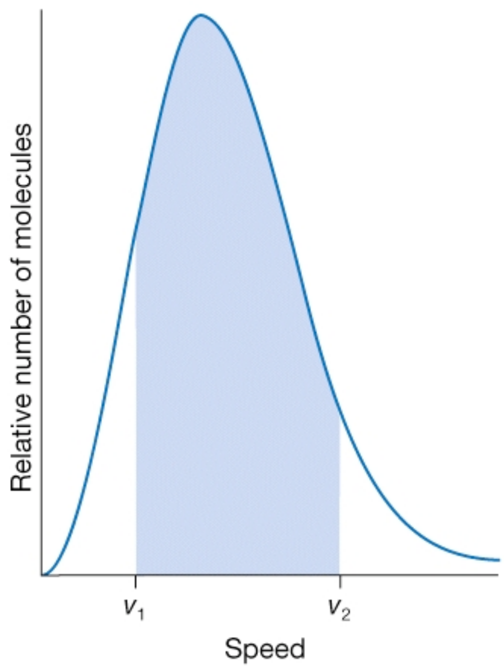
The area under the Maxwell distribution curve increases with decreasing temperature.

Application of the Maxwell Distribution 1: Mean speed

Calculate the **mean speed ($\bar{c}$)** of molecules in O_2 gas at 25°C, 1 bar.



Application of the Maxwell Distribution 2: Finding the proportion of molecules traveling at a certain range of speeds:



$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \exp\left(-Mv^2/2RT\right)$$

- It is not correct to simply "plug in" values to determine how many nitrogen molecules travel with a particular speed v.
- Instead we must evaluate $f(v)dv$ (or $f(v)\Delta v$), not simply $f(v)$.

Example: At 500 K, what fraction of nitrogen molecules travel with speeds between 290 and 300 m s^{-1}?

$$fraction^{500K} = \int_{290ms^{-1}}^{300ms^{-1}} f(v)dv$$

Useful trick: If the fraction of the population that we are considering is very small, then $f(v)$ is approximately constant over the limits of integration.

If we assume $f(v)$ is constant over the range $v = 290$ to $300\ \text{m s}^{-1}$, we can use $v = 295\ \text{m s}^{-1}$ to calculate the fraction of N_2 traveling at this speed range:

We can check the assumption that was used to obtain this answer:

$$f(290ms^{-1}) = 4\pi\left(\frac{28.02\times 10^{-3}\,kg\,mol^{-1}}{(2\pi)(8.314JK^{-1}mol^{-1})(500K)}\right)^{3/2} \times \left(290ms^{-1}\right)^2 \times \exp\left((-3.37\times 10^{-6})(290)^2\right)$$

$$= 4\pi\left(\frac{3.37\times 10^{-6}m^{-2}s^2}{\pi}\right)^{3/2} \times \left(290ms^{-1}\right)^2 \times \exp\left((-3.37\times 10^{-6})(290)^2\right)$$

$$= 8.84\times 10^{-4}m^{-1}s$$

$$f(300ms^{-1}) = 4\pi\left(\frac{28.02\times 10^{-3}\,kg\,mol^{-1}}{(2\pi)(8.314JK^{-1}mol^{-1})(500K)}\right)^{3/2} \times \left(300ms^{-1}\right)^2 \times \exp\left((-3.37\times 10^{-6})(300)^2\right)$$

$$= 4\pi\left(\frac{3.37\times 10^{-6}m^{-2}s^2}{\pi}\right)^{3/2} \times \left(300ms^{-1}\right)^2 \times \exp\left((-3.37\times 10^{-6})(300)^2\right)$$

$$= 9.28\times 10^{-4}m^{-1}s$$

Note: $f(295\ \text{m s}^{-1})$ = the average of $f(290\ \text{m s}^{-1})$ and $f(300\ \text{m s}^{-1})$

Application of the Maxwell Distribution 3: Most probable speed (*c)**

- This represents the *maximum* of $f(v)$.
- To find the maximum of a function take the derivative and set it equal to zero.

$$\frac{df(v)}{dv} = 0$$

$$\frac{d\left[4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \exp\left(\frac{-Mv^2}{2RT}\right)\right]}{dv} = 0$$

$$2v\exp\left(\frac{-Mv^2}{2RT}\right) + v^2\left(\frac{-Mv}{RT}\right)\exp\left(\frac{-Mv^2}{2RT}\right) = 0$$

Summary of the molecular speed equations from the Maxwell Distribution

What does each equation tell us?

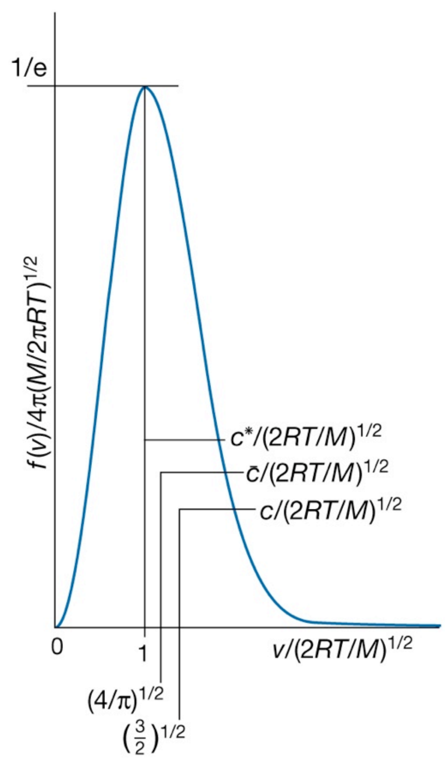
$$c = \sqrt{\frac{3RT}{M}} \qquad \bar{c} = \sqrt{\frac{8RT}{\pi M}} \qquad c^* = \sqrt{\frac{2RT}{M}}$$

Plus: The relative mean speed (the mean speed with which one molecule approaches another):

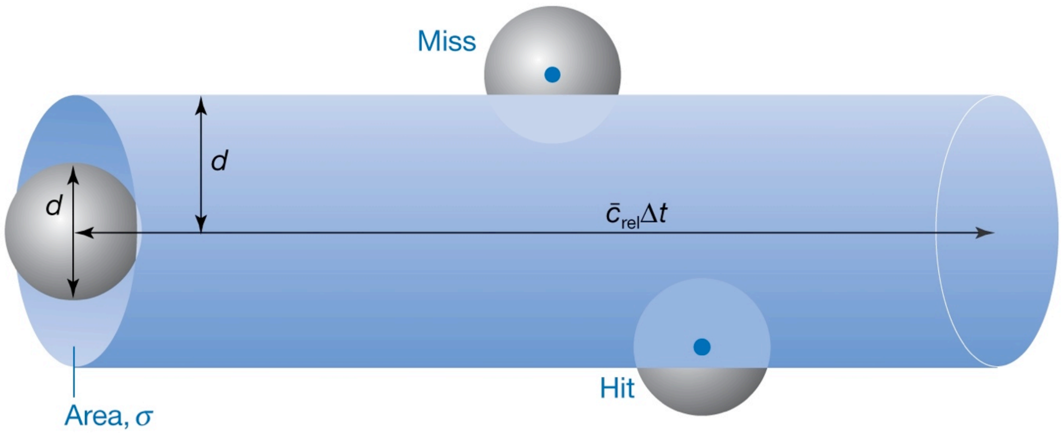
$$\bar{c}_{rel} = \sqrt{\frac{8kT}{\pi\mu}}$$

$$\bar{c}_{rel} = \sqrt{2}\left(\bar{c}\right)$$

when $m_A = m_B$.



What is the collision frequency?



- a collision occurs if the centers of two molecules come within distance *d* of each other.
- collision tube has cross-sectional area $\sigma = \pi d^2$ and length $\bar{c}_{rel}\Delta t$, hence

$$V_{\text{Collision Tube}} = \sigma \bar{c}_{rel}\Delta t$$

- the concentration of molecules in this collision tube can be expressed as the number density $\boldsymbol{N}$:

$$\boldsymbol{N} = \frac{N}{V} \text{ (number of molecules } N \text{ per unit volume } V\text{)}$$

- therefore:

$$\text{\# of stationary molecules in the collision tube} = \boldsymbol{N}\sigma \bar{c}_{rel}\Delta t$$

$$= \textit{the number of collisions which occur during } \Delta t$$

- the number of collisions per unit time is the collision frequency (z):

$$z = \boldsymbol{N}\sigma \bar{c}_{rel}$$

In terms of pressure and temperature:

For a nitrogen molecule in a sample at 1 atmosphere and 298 K, $z = 5 \times 10^9$ s^{-1}, meaning that a given molecule experiences a collision about 5000000000 times per second!

Concept Check: True or False?

1. At constant temperature the collision frequency increases with increasing pressure.

2. At constant volume, the collision frequency increases with increasing temperature.

The mean free path: How far does a molecule travel between collisions?

For a collision frequency z, a molecule spends a time $1/z$ in "free flight" between collisions and travels a distance called the "mean free path" (λ) during this time:

$$\lambda = \frac{\bar{c}}{z}$$

We may substitute the previous expression for z to get:

$$\lambda = \frac{kT}{\sqrt{2}\sigma P}$$

Typical numbers for N_2 gas at 1 atm, 298 K:

- Mean speed ~ 500 m s^{-1}
- ~1 collision every ns
- mean free path = 70 nm
- a single molecule will on average travel 1000 times its molecular diameter between collisions

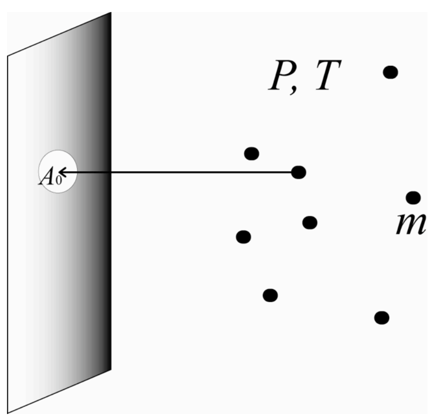
Does N_2 gas at 298 K, 1 atm follow the assumptions used to come up with the kinetic theory of gases (page 1)?

Collisions with walls and surfaces

- We have seen how the Maxwell Distribution function can be used to calculate molecular speeds, and therefore rates of collisions between molecules, an important factor in gas-phase chemical reactions.
- Another useful property that comes from this function is the **collision flux** (Z_W)
  - *i.e.* the number of collisions with a given surface area in a given time.

$$Z_W = \frac{p}{\sqrt{2\pi mkT}}$$

- Derivation available in Justification 20.4 (for those who are interested…)
- This provides a measure of the transport properties of a gas.
- Z_W is also an important factor in surface chemistry
- Z_W can be used to obtain the collision frequency, z, by multiplying Z_W with the surface area undergoing the collisions
- This can be used to determine the rate of **effusion**
  - i.e. the emergence of a gas from a container through a small hole



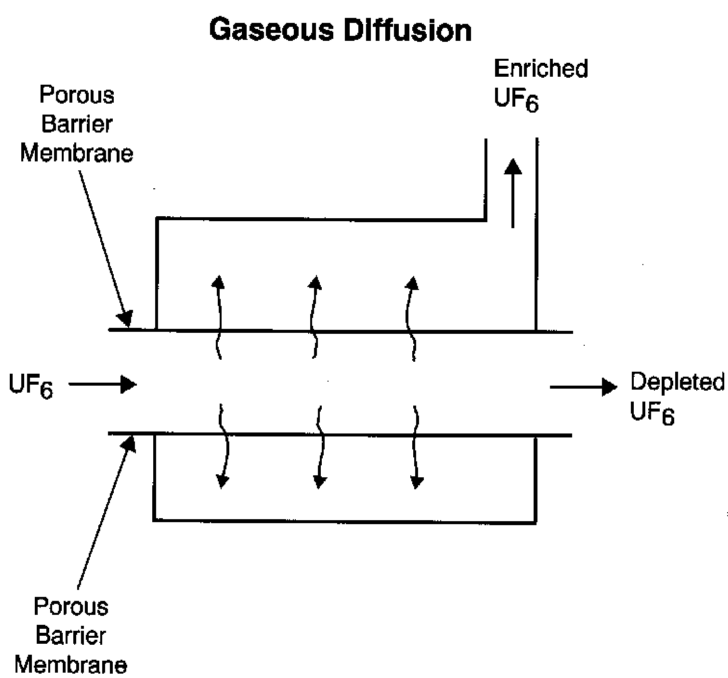
Can you come up with an equation for the effusion of a gas through an opening of area A_o? (Hint: The answer is provide in the text above!)

Graham's law of effusion

- Thomas Graham was intrigued by a report that hydrogen gas diffused out through a crack in a broken container faster than the air from the surroundings diffused in to replace it
- He devised experiments to allow precise experimental measurement of diffusion rates for gases
    - e.g. measured the rate of loss from a container through thin long tube
- found that the rate of effusion is inversely proportional to the square root of the molar mass.

Does Graham's law agree with the kinetic theory of gases?

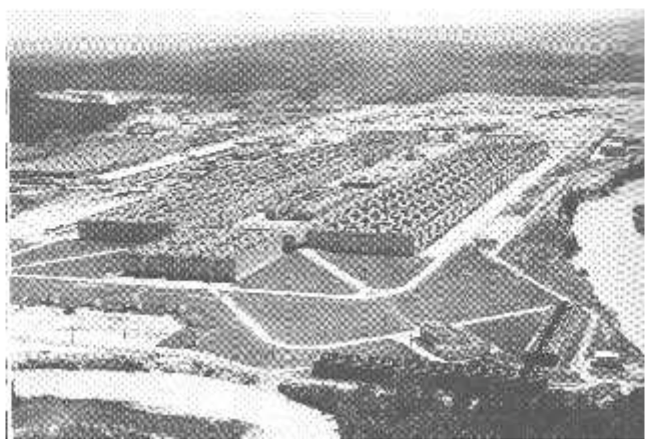
Application of Graham's Law: Uranium Enrichment



http://www.chemcases.com/2003version/nuclear/nc-07.htm

The principle of effusion was used in the Manhattan Project to produce U-235 enriched uranium hexafluoride, UF_6.

By the spring of 1945, Oak Ridge had shipped approximately 132 lbs. of enriched uranium (approximately 90% U-235, 10% U-238) to Los Alamos, New Mexico. This was used in "Little Boy", the bomb dropped on Hiroshima on August 6, 1945. The majority of fission weapons since that time have used plutonium.
Uranium hexafluoride (UF_6), the gaseous compound of uranium, is used in this process. Since there is only one common isotope of fluorine, F-19, the ratio of rates of effusion becomes:



K-25 Gaseous Diffusion Plant, Oak Ridge, TN
(Courtesy of the Department of Energy)

This small difference in rates means that many effusion barriers (stages) are necessary for enrichment. The K-25 gaseous diffusion plant at Oak Ridge required 4000 stages. This plant was one-half mile long and six stories high and covered 43 acres. The production of a suitable barrier was the key to successful separation. The holes must be microscopic (approximately one-millionth of an inch in diameter) and uniform in size. The porosity must always be high to sustain high flow rates and the barrier must not react with the highly corrosive hexafluoride. Nickel and aluminum oxide were best suited for barrier materials.

Uranium enrichment is currently used to produce fuel (3 to 4% U-235) for civilian nuclear reactors.