

## Announcements – 10/9/00

- **Note:** Additional readings and problems in Chapter 11!
- **Quiz Today**
- **Exam #2:** *Wed., 10/18, 7:00 pm*  
-contact me THIS WEEK if you need to schedule an alternate time
- **Demo today!**

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## Graham's Law of Effusion

If gas molecules are allowed to enter a vacuum only through a small opening:

The rate at which they *effuse* through the opening will vary with the *square root* of their molar masses:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$



So that's why those cheap helium-filled balloons don't last very long! <sup>2</sup>

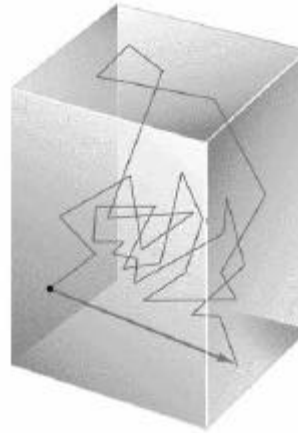
# Diffusion

- *Diffusion* is the spread of a substance through space (or through another substance)

-gas molecules travel in a straight line until they collide with something, after which, they *change direction*

-the *distance* that they travel before they collide is called the **mean free path (mfp)**

-*mfp varies with density:*  
nm @ atm pressure  
cm @ upper atmosphere



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# What about individual gas particles?

- We can also express the *average kinetic energy* per particle in terms of temperature. For 1 mol:

$$\langle \epsilon_k \rangle = \frac{\text{Total Kinetic Energy}}{\# \text{ particles}} = \frac{E_k}{N_0} = \frac{3/2 RT}{N_0}$$

$$\langle \epsilon_k \rangle = 3/2 k_B T$$

↖ Boltzmann's Constant  
(= 1.38066 x 10<sup>-23</sup> J/K)

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# Maxwell-Boltzmann Statistics

- Allows us to characterize the behavior of *individual particles* by statistical analysis of the *aggregate*
- The speed distribution for a gas at thermal equilibrium:

$$F(v) = Kv^2e^{-mv^2/2k_bT}$$

where:  $K = 4\pi(m/2\pi k_b T)^{3/2}$  - constant at fixed temp

There are two opposing trends:

$$F(v) \propto v^2 \text{ (incr)} \quad \text{AND} \quad F(v) \propto e^{-v^2} \text{ (decr)}$$

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# Maxwell-Boltzmann Speed Distribution

## Example: Argon

$$T_1 = 273.15 \text{ K}$$

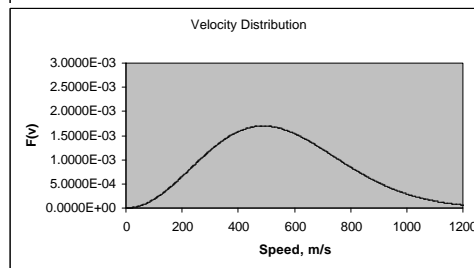
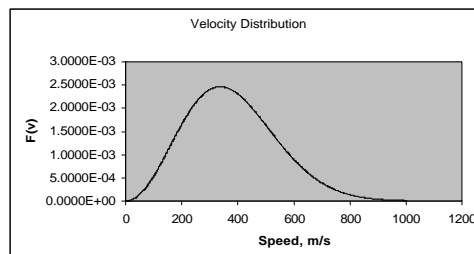
$$v_{\text{rms}} = 413.0 \text{ m/s}$$

$$v_{\text{mp}} = 337.2 \text{ m/s}$$

$$T_2 = 573.15 \text{ K}$$

$$v_{\text{rms}} = 598.2 \text{ m/s}$$

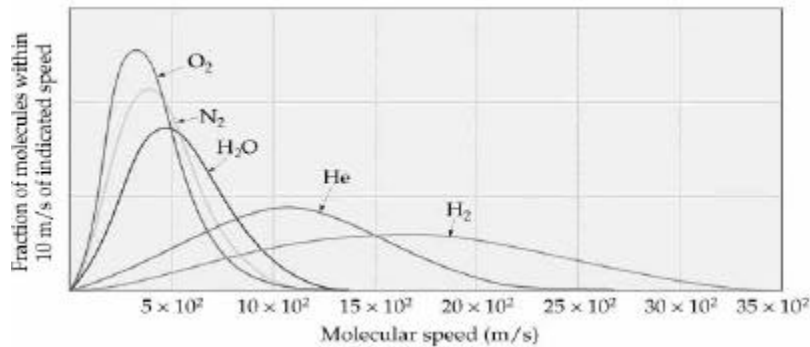
$$v_{\text{mp}} = 488.4 \text{ m/s}$$



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## Maxwell-Boltzmann: Effect of Gas Composition

- Avg Kinetic Energy is *independent of gas composition* @ depends **only** on temperature
  - since the **mass** of the gas molecules varies with composition, the **velocities of the molecules** must vary with composition:



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## NON-Ideal Gases: The *Real* Thing

- If a gas acts *ideally*:

$$\frac{PV}{RT} = 1 \quad \text{for 1 mol gas}$$

- A plot of  $\frac{PV}{RT}$  versus P should yield a straight line at a constant value of 1.00

*Let's take a look, shall we?*

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## Real Gas Behavior

➤ No deviations until  $P > 20$  atm

➤ Negative Deviations at intermediate pressures

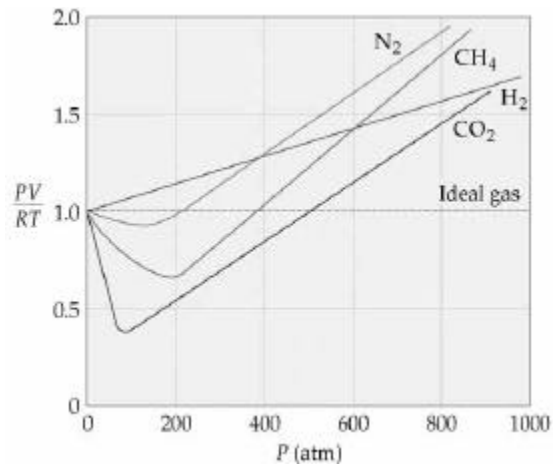
➤ Due to lower than *ideal* volumes

➤ Molecular **attractions**

➤ Positive Deviations at high pressures

➤ Due to higher than *ideal* volumes

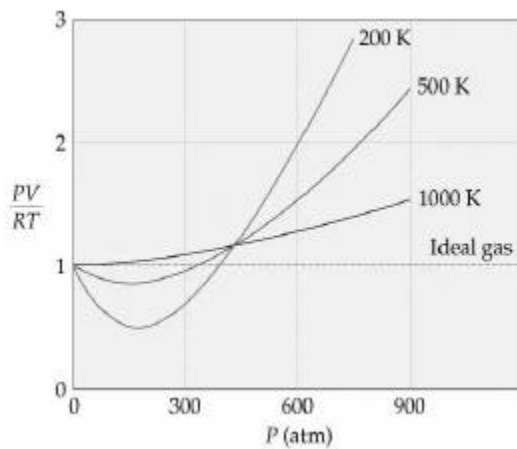
➤ Molecular **repulsions**



At constant temperature (300 K)

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## Effect of Temperature



-negative deviations are more significant at lower temps

-due to decreased molecular motion, allowing more significant intermolecular interactions

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