CHEM 116
Characterizing Gas Behavior Mathematically

Lecture 2
Prof. Sevian

Today's agenda

- Some uses of the ideal gas equation
  - Typical gas law problems
  - Density ("mass density") of gases
  - Molar mass determination
  - Stoichiometry
- How gas behavior is measured in the lab
- Temperature distributions
- Kinetic molecular theory, and how it leads to the combined gas law
- Graham's law of effusion
- Partial pressures
- Vapor pressure experiments
- When the assumptions fail: non-ideal behavior

Note: We probably won't get through all of the items on this list during Lecture 2.
What we don't get to in Lecture 2 will be covered in Lecture 3.

Announcements

FSG's

- FSG's will start the week of Sept 15
- Shainaz Landge (FSG facilitator) will visit our class on Tues Sept 9 to give out a survey and find out what are the best two times for you
- I'll let you know the results of her survey on Thurs Sept 11, and will also post the info on the course website

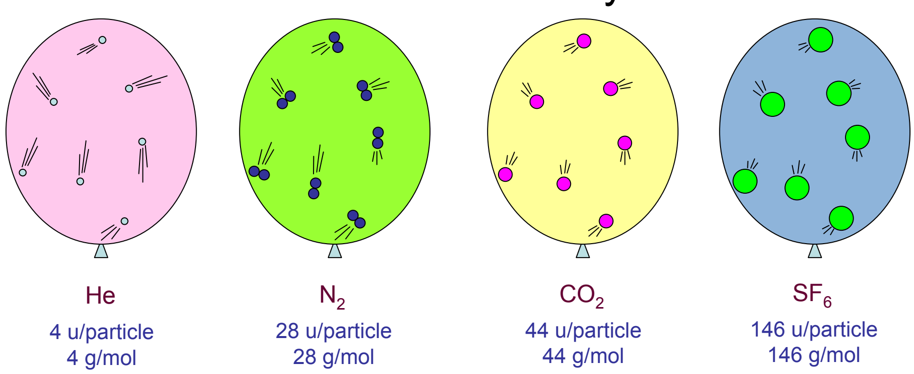
Pre-test

- You will take the pre-test during the first hour of lab on either Mon Sept 15 or Weds Sept 17
- If you are not enrolled in Chem 118, please attend lab for the first hour (1:00-2:00 in S-2-35) either one of these days to take the pre-test
- If you can't take the pre-test at lab, please make arrangements with me to take the pre-test sometime during the week of Sept 15. After that week is up, it will not be possible to take the pre-test and you will get 0 out of 10 points for the pre-test grade.

Freshman chemistry major advising

- If you are a freshman and a chemistry major, please attend the meeting for freshman chemistry majors with your advisor, Prof. Dransfield, at 4:00 today in the chemistry conference room (S-1-89). See signs posted on the door of this lecture hall for more info.

Balloon Quandary

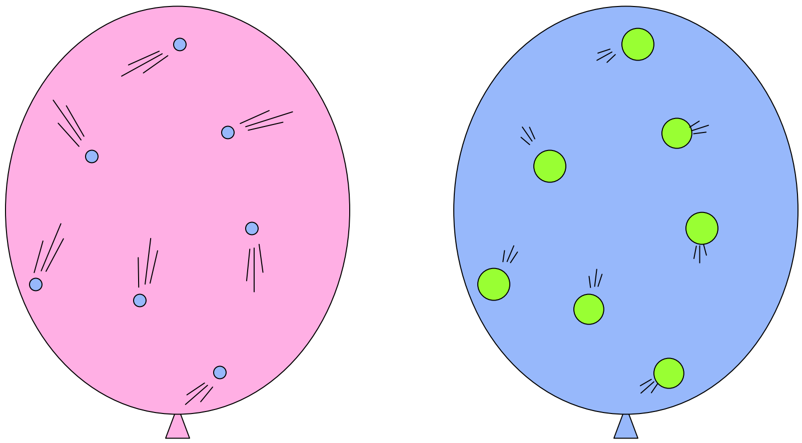


- All four balloons have the same volume and temperature, and are under the same conditions of pressure.
- Assume the temperature is T = 298 K, the volume is V = 2.00 L, and the pressure is p = 1.00 atm. The value of R to use is 0.08206 L·atm/mol·K.
  - How many moles (n) of He are in the He balloon?
  - Figure out n for the other three balloons.

Please turn in Clicker Quiz #1 at the beginning of class (Thurs Sept 4)

Particle density vs. Mass density

The balloons all have the same particle density. Why does the SF_6 balloon weigh more than the other balloons?



Mass Density

$$D = \frac{m}{V} = \frac{m}{\left(\frac{nRT}{p}\right)} = \frac{mp}{nRT} = \left(\frac{m}{n}\right)\left(\frac{p}{RT}\right) = M\left(\frac{p}{RT}\right)$$

Density of N_2 at room temp

T = 298K

p = 1.00 atm

M_w = 28.0 g/mol

$$D = M\frac{P}{RT}$$
$$= \left(28.0\frac{g}{mol}\right)\frac{(1.00atm)}{\left(0.08206\frac{L \bullet atm}{mol \bullet K}\right)(298K)}$$
$$= 1.15\, g/L$$

Density of SF_6 at room temp

T = 298K

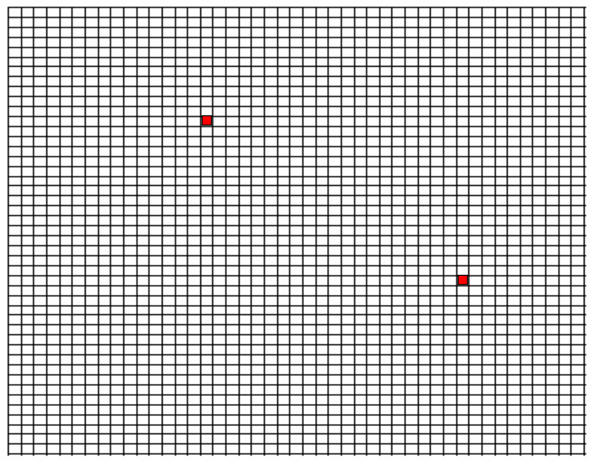
p = 1.00 atm

M_w = 146 g/mol

$$D = M\frac{p}{RT}$$
$$= \left(146\frac{g}{mol}\right)\frac{(1.00atm)}{\left(0.08206\frac{L \bullet atm}{mol \bullet K}\right)(298K)}$$
$$= 5.97\, g/L$$

A note about accuracy of the pictures (i.e., “not drawn to scale”)

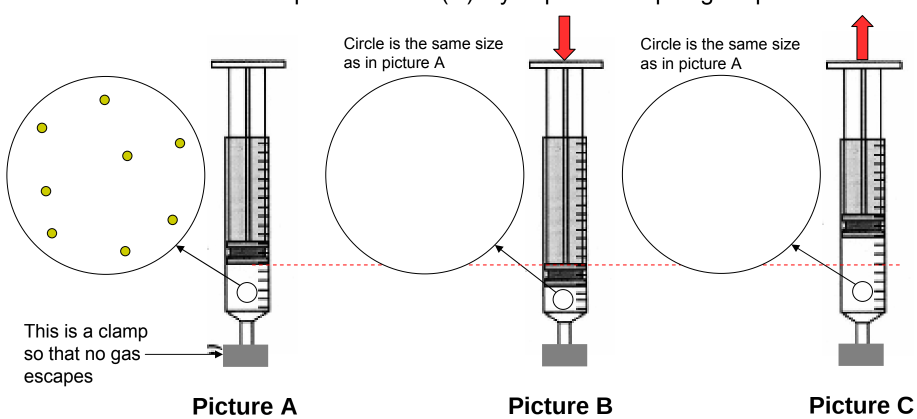
A more accurate depiction: 1 in 1000 at room temperature



Conceptualizing particle density

Imagine placing a syringe into a balloon filled with Argon and filling the syringe with that gas, then clamping it shut. Now, imagine you have a magic microscope that is so strong that you can see individual gas particles.

- Picture A depicts the argon particles in a small part of the syringe barrel.
- How would the particles look (B) if you pushed the plunger down?
- How would the particles look (C) if you pulled the plunger up?



Examples of use of ideal gas equation

1. A helium balloon is inflated until it's nearly full (2.0L) in a toy store that is air conditioned to 20ºC on a day when it is standard pressure outside. The customer takes the balloon outdoors where it is 36ºC. The maximum capacity of the balloon is 2.1L. Will it burst?

2. Calculate the molar mass of a vapor that has a density of 7.135 g/L at 12ºC and 743 torr.

3. How many liters of hydrogen gas at STP would be generated by completely reacting 2.55 g of Zn metal in the following reaction?
   $Zn\ (s) + 2\ HCl\ (aq) \rightarrow H_2\ (g) + ZnCl_2\ (aq)$

Key ideas about the behavior of gases

- Because all gases behave similarly, the same mathematical model can be used to predict their behavior
- The model rests on these assumptions:
  - Gas particles are so widely separated that they do not attract or repel each other
  - Gas particles are in ceaseless random rapid motion, so their behavior can be explained as averages over lots of particles

Key points so far

- The gas state is one state of matter. It is the easiest state to study because it is possible to make the assumption that gas particles do not interact with each other.
- The "ideal gas" is a model. Ideal gases are pretend gases, but the ideal gas law does a pretty good job of predicting gas behavior, under certain conditions.
- If real gases are behaving like ideal gases, and if they don't interact with each other, then two gases that fill the same volume at the same temperature must be present in equal molar quantities. They have the same particle density, but different mass densities.

New Quandary Today about the Balloons

Between last class and now:

- the SF_6 balloon to got bigger
- the He balloon got smaller
- the N_2 and CO_2 balloons stayed about the same, though the CO_2 balloon was a little bigger than the N_2 balloon

What's going on at the particle level?

and/or

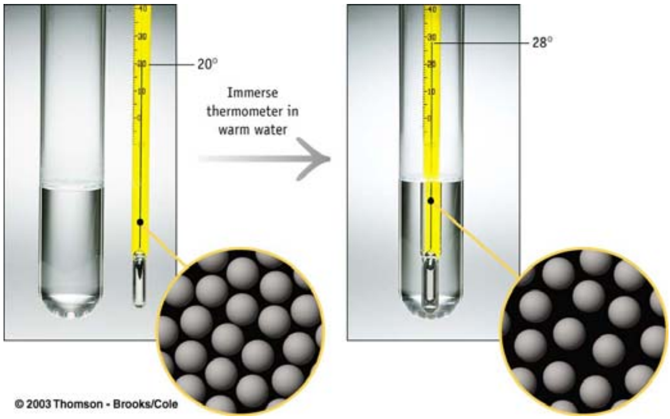
How can this be explained with a mathematical model?

Measuring gases

- Number of particles
  - Quantity: ***n*** (moles)
  - Can be converted from/to mass (grams)
- Volume (space) that the gas occupies
  - Three dimensional space: ***V*** (liters)
  - Could be given in other units: mL, m^3, cm^3
- Temperature
  - A measure of the motion of particles: ***T*** (degrees Kelvin)
  - Could be given in other units: ºC
- Pressure
  - Force per unit area: ***p*** (atm)
  - Also used in other units: kPa, Pa, mmHg, torr

Temperature

- A measurement made using an instrument called a thermometer
- How it works:

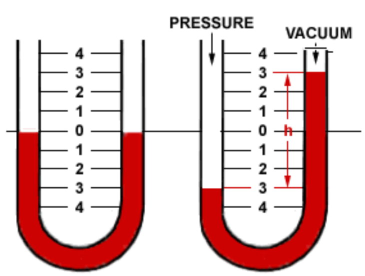


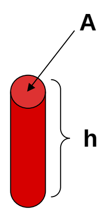
- So, what does temperature measure?

Relative vs. Absolute Temperature Scales

- Relative temperature (linear) scale measures temperature of an object relative to two points
  - Coldest and warmest temperatures at which humans can typically survive → Fahrenheit scale is relative
  - Freezing and boiling points of water → Celsius scale is relative
- Absolute temperature (linear) scale measures absolute motion of particles → Kelvin scale is absolute
  - Absolute zero temperature is a point of reference for disorder: there is no disorder at zero (Third Law of Thermodynamics)
  - Convenience: the size of 1 ºC is equal to the size of 1 K

Pressure





V=Ah

so A = V/h

Pressure is defined as force per unit area.

$$p = \frac{F}{A} = \frac{mg}{V/h} = \left(\frac{m}{V}\right)gh = Dgh$$

Pressure is measured as mmHg in a mercury manometer (vacuum in closed end)

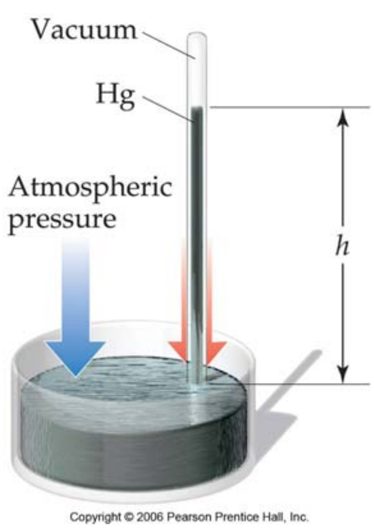
How a manometer works

A manometer measures pressure by allowing gravity and gas pressure to cause a height difference in a U-shaped tube of mercury

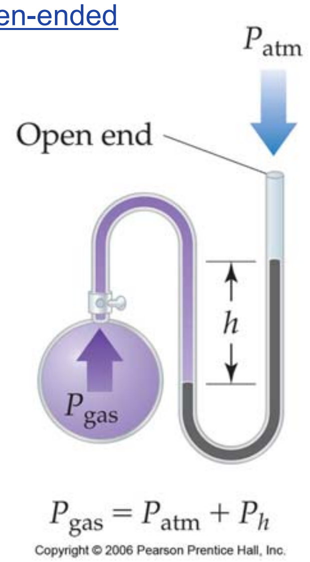
http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/gaslaw/manometer5.swf

Two kinds of manometers

Closed-ended



Open-ended



Key points so far about gases

- pV/nT = constant
- $pV = nRT$ (ideal gas law)
- At STP, the molar volume of a gas is 22.4 L/mol
- Ideal gas law rests on assumptions. Model works best when a gas is under conditions that come closer to assumptions being true.
- Celsius and Kelvin temperature scales:
  - Same degree sizes, Kelvin is shifted 273.15 degrees higher than Celsius
  - Different in that Celsius is relative to water freezing point, Kelvin is absolute temperature scale (zero Kelvin means velocities of all particles equal zero)
- **Always use Kelvin in gas law model/calculations!**

Key ideas about the behavior of gases

- Because all gases behave similarly, the same mathematical model can be used to predict their behavior
- The model rests on these assumptions:
  - Gas particles are so widely separated that they do not attract or repel each other
  - Gas particles are in ceaseless random rapid motion, so their behavior can be explained as averages over lots of particles

Assumptions we can make about gases to build a model (Kinetic Molecular Theory)

1. No attractive forces between gas particles
2. Volume of individual particles is negligible compared to volume occupied by the gas
3. Particles are in constant motion
4. Particle travel in straight lines and change velocities only when they collide, either with other particles or with walls of container – all collisions are elastic (no loss of kinetic energy)
5. Pressure arises from particles hitting walls of container
6. Average kinetic energy is proportional to the temperature of the gas

What does the distribution of speeds of the particles in a gas look like?

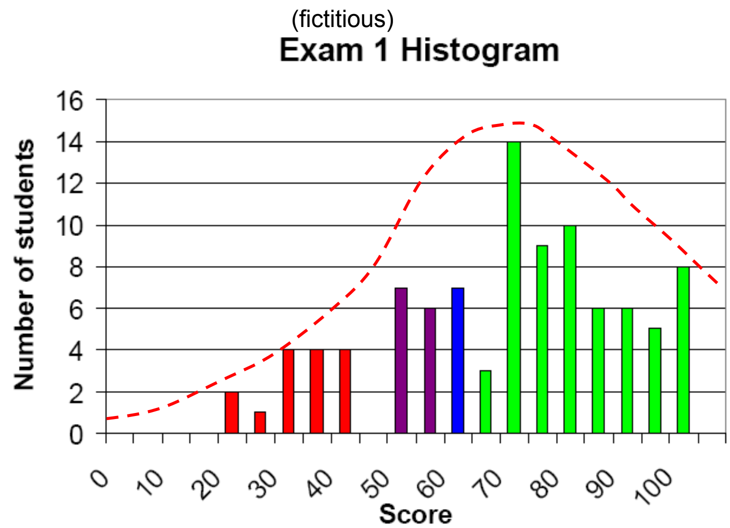
Animation of He and Ne gases at where you can control *P, T, n* and *V*, and then watch how the system responds

http://intro.chem.okstate.edu/1314F00/Laboratory/GLP.htm

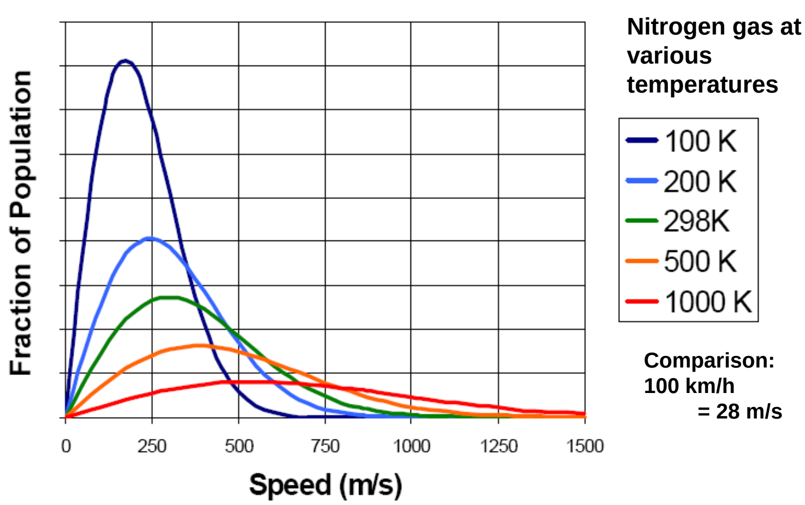
If you want to repeat at home what I will show in class:

- Set it up with constant pressure
- Make the volume really large and place the maximum number of particles in it so you can get a better statistical spread
- Enable "tracking" of the tagged particle if you'd like to watch the red-tagged particle whose velocity changes as it collides
- Observe the distribution of velocities of He particles
- Change the temperature – how does the distribution change?
- Try looking at the same number of Ne particles, same volume, same temperature – how is the velocity distribution different from He?

Distribution of grades on an exam

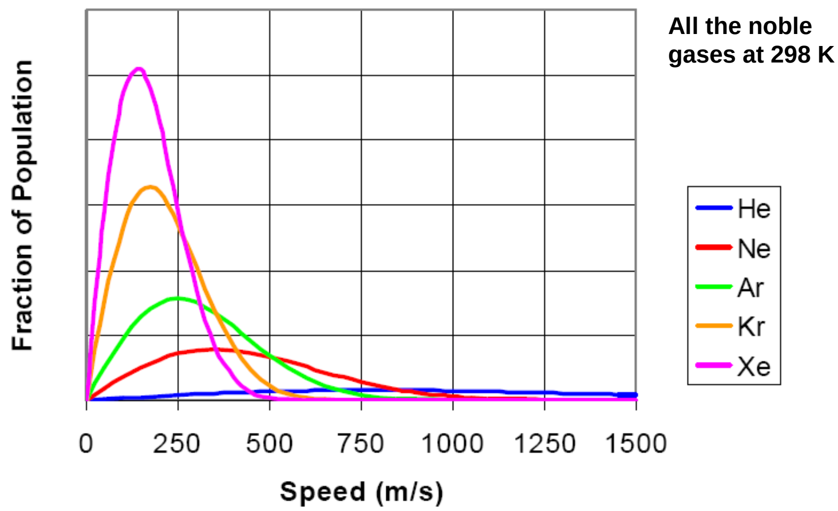


Distribution of speeds of particles in a gas



What can you conclude?

Distributions for different gases at the same temperature



What can you conclude?

Conclusions about behavior of gas particles

1. In any gas, there is a wide distribution of the speeds of particles
2. As the temperature increases, particles move faster on average
3. As the temperature increases, the distribution of speeds is larger
4. At the same temperature, different gases have different average speeds
   - Heavier gas particles move slower on average
   - Lighter gas particles move faster on average

Average velocity vs. Root mean square velocity

Average velocity

$$v_{\text{avg}} = \frac{\sum_{i=1}^{i=N} v_i}{N} = \frac{v_1 + v_2 + \ldots + v_N}{N}$$

Root mean square velocity

$$v_{\text{rms}} = \sqrt{\frac{\sum_{i=1}^{i=N} v_i^2}{N}} = \sqrt{\frac{v_1^2 + v_2^2 + +\ldots\ v_N^2}{N}}$$

$$v_{\text{avg}} = 0.921 \times v_{\text{rms}}$$

Which one is a measure of average kinetic energy? $KE = \frac{1}{2}mv^2$

KMT prediction of r.m.s. speed of a gas

$$\boxed{v_{rms} = \sqrt{\frac{3RT}{M}}}$$

Does the equation make sense?

- What happens to average speed when temperature increases?
- What happens to average speed when mass increases?
- How does the kinetic energy vary with temperature?

$$KE = \frac{1}{2}Mv^2 = \frac{1}{2}M\frac{3RT}{M} = \frac{3}{2}RT$$

- Do the units make sense?

$$Joules = (kg)\left(\frac{m}{s}\right)^2 = \frac{kg \bullet m^2}{s^2}$$

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

$$\frac{m}{s} \stackrel{?}{=} \sqrt{\frac{3\left(8.314\frac{J}{mol \bullet K}\right)(T \text{ in } K)}{\text{M in } \frac{kg}{mol}}}$$

$$= \sqrt{\frac{3\left(8.314\frac{kg \bullet m^2/s^2}{mol \bullet K}\right)(T \text{ in } K)}{\text{M in } \frac{kg}{mol}}}$$

Practical uses of KMT model

1. Different gases have different average speeds, so they “effuse” differently (remember our balloons)
   - Useful for identifying gases

2. In a mixture of gases, all gases spread out to occupy the entire volume
   - Useful for measuring how much gas is produced during a reaction

Today’s quandary

Question was: Why did the following happen?

- the SF_6 balloon to got bigger
- the He balloon got smaller
- the N_2 and CO_2 balloons stayed about the same, though the CO_2 balloon was maybe a little bigger than the N_2 balloon

Explain what’s going on at the particle level

and/or

Explain mathematically

Graham's law of effusion

- Effusion is the escape of gas through a tiny hole in a container
- What happens as the particles have larger and larger mass?
- http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/gaslaw/effusion_macro.swf
- This behavior is predicted by KMT

$$T_A = T_B \quad \text{so} \quad KE_A = KE_B$$

$$\text{and therefore,} \quad \frac{1}{2}m_A v_A^2 = \frac{1}{2}m_B v_B^2$$

rearranging,

$$\frac{v_A^2}{v_B^2} = \frac{m_B}{m_A} \quad or \quad \frac{v_A}{v_B} = \sqrt{\frac{M_B}{M_A}}$$

alternative:

$$v_A = \sqrt{\frac{3RT}{M_A}} \quad and \quad v_B = \sqrt{\frac{3RT}{M_B}}$$

$$\text{therefore} \quad \frac{v_A}{v_B} = \sqrt{\frac{\frac{3RT}{M_A}}{\frac{3RT}{M_B}}} = \sqrt{\frac{M_B}{M_A}}$$

Ways to read Graham's law

$$\boxed{\frac{v_A}{v_B} = \sqrt{\frac{M_B}{M_A}}}$$

- Speeds of particles
  - Ratio of speeds in inverse proportion to square root of molar masses
  - If molar mass of B is larger than molar mass of A, then speed of A is faster than speed of B by the inverse ratio of the square roots of the molar masses
- Rates of effusion
  - Rate of "leakage" of gas out of a hole is proportional to r.m.s. speed of gas particles
- Time to effuse
  - The faster the speed, the shorter the time
  - Times are opposite (mathematical inverse of) rate or speed

Today's quandary

Question was: Why did the following happen?

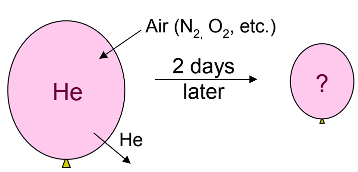
- the SF_6 balloon to got bigger
- the He balloon got smaller
- the N_2 and CO_2 balloons stayed about the same, though the CO_2 balloon was maybe a little bigger than the N_2 balloon

Explain what's going on at the particle level

and/or

Explain mathematically

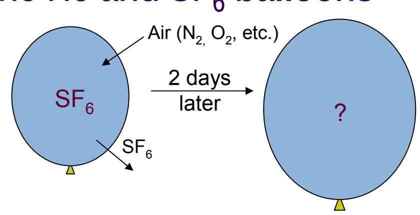
Compare what happened to the He and SF_6 balloons



- During the two days, which gases effused across the porous barrier of the latex balloon?
- In what direction?
- Compare the rates of effusion

$$\frac{v_{He}}{v_{N_2}} = \sqrt{\frac{M_{N_2}}{M_{He}}} = \sqrt{\frac{28}{4}} = 2.65$$

- So He effuses out 2.65 times faster than N_2 effuses in



- Which gases effused across the porous barrier?
- In what direction?
- Compare the rates of effusion
- Which gas effuses faster, SF_6 or N_2? How much faster?

What use is Graham's law?

Example:

A sample of pure methane, CH_4, is found to effuse through a porous barrier in 1.50 min. Under the same conditions, an equal number of molecules of an unknown gas effuses through the barrier in 4.73 min. What is the molar mass of the unknown gas?

Key points from today

- *pV/nT* = constant
- *pV* = *nRT* (ideal gas law)
- At STP, the molar volume of a gas is 22.4 L/mol
- Ideal gas law rests on assumptions. Model works best when a gas is under conditions that come close to assumptions being true.
- Celsius and Kelvin temperature scales:
  - Same degree sizes, Kelvin is shifted 273.15 degrees higher than Celsius
  - Different in that Celsius is relative to water freezing point, Kelvin is absolute temperature scale
- Always use Kelvin in gas law model/calculations
- If collecting a gas over water, the gas collected includes both the product of interest and water vapor