## **CHEM 116** The Ideal Gas Model: Its Usefulness and Conditions Where it Breaks Down

Lecture 3 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

Last Thursday

- 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 Today
  - Partial pressures
  - Vapor pressure experiments
  - When the assumptions fail: non-ideal behavior

Note: Hopefully we will get through the rest of Chapter 10 (Gases) today. I have included some of Chapter 11 (Intermolecular Interactions) at the end.

### Announcements

#### FSG's

- FSG's will start the week of Sept 15
- Shainaz Landge (FSG facilitator) will visit our class today at the end of class 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 in
- M-1-417 from 1:00-2:00. Since this is at the very beginning of lab, you can go directly to the classroom in McCormack first.
- If you are not enrolled in Chem 118, please attend lab for the first hour (1:00-2:00) 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.

#### i>Clickers

- On Thursday we will begin using i>clickers. If you own a clicker, bring it to class with you
  every day, starting this Thursday.
- If you do not own a clicker, I will loan you one. You must come by my office (W-4-181) to get it tomorrow or after tomorrow. If you do not return it to me at the end of the semester, you will receive an INC for the course. If you lose it, you can buy another one on amazon.com for around \$30.

# Example of what a clicker question can look like in this course



## Which of the following statements about distributions of speeds of particles in a gas is true?

- I. In a gas at a particular temperature, all of the particles move at the same speeds.
- I. If two different gases are at the same temperature, they have the same distributions of particle speeds.
- III. For the same gas, the distribution of particle speeds at a higher temperature is more spread out and has a higher average than the distribution at a lower temperature.
- (A) All of them are true
- (B) Only II is true
- (C) II and II are true
- (D) Only III is true
- (E) I and III are true

# 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  

$$v_{\text{avg}} = \frac{\sum_{i=1}^{i=N} v_i}{N} = \frac{v_1 + v_2 + \dots + v_N}{N}$$
Root mean square velocity  

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

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

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

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

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

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

## Practical uses of KMT model

Different gases have different average speeds, so 1. they "effuse" differently (remember our balloons)

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S

- 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

### Last Thursday's quandary

Question was: Why did the following happen?

- the SF<sub>6</sub> balloon to got bigger
- the He balloon got smaller
- the N<sub>2</sub> and CO<sub>2</sub> balloons stayed about the same, though the CO<sub>2</sub> balloon was maybe a little bigger than the N<sub>2</sub> balloon

#### Explain what's going on at the particle level

#### and

Explain mathematically



### Graham's law of effusion

Extra credit challenge (up to 3 points) What are the molecular weights (molar masses) of gas X, gas Y, and gas Z in the animation linked on this page? Due at beginning of next class (9/11).

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

$$T_{A} = T_{B} \text{ so } KE_{A} = KE_{B}$$
  
and therefore,  $\frac{1}{2}m_{A}v_{A}^{2} = \frac{1}{2}m_{B}v_{B}^{2}$   
rearranging,  
 $\frac{v_{A}^{2}}{v_{B}^{2}} = \frac{m_{B}}{m_{A}} \text{ or } \frac{v_{A}}{v_{B}} = \sqrt{\frac{M_{B}}{M_{A}}}$  therefore

alternative :

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

#### Ways to read Graham's law



- 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

#### Compare what happened to the He and SF<sub>6</sub> balloons



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

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

• So He effuses out 2.65 times faster than N<sub>2</sub> effuses in



- Which gases effused across the porous barrier?
- In what direction?
- Compare the rates of effusion
- Which gas effuses faster, SF<sub>6</sub> or N<sub>2</sub>? 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?

#### **Gas mixtures**

- All gases in a mixture spread out to occupy the entire space available
- Each component gas behaves as if it alone occupied the entire volume (which assumption of KMT supports this?)
- Each component exerts its own partial pressure, such that the sum of the partial pressures equals the total pressure
- Dalton's law of partial pressures

$$p_{total} = p_A + p_B + p_C + p_D + \dots = \sum_i p_i$$

### More about partial pressures



For vapor pressures of water at different temperatures, see Appendix B in your text, p. 1122



Total pressure inside must equal sum of partial pressures of water vapor and the gas being collected:  $p_{atm} = p_{water} + p_{gas}$ 

## Collecting a gas over water

For vapor pressures of water at different temperatures, see Appendix B in your text, p. 1122. In this table, at 25°C, the vapor pressure of water is 23.76 torr.

#### Example similar to additional question on Assignment 2

Zinc is reacted with excess hydrochloric acid in a vessel in such a way that the hydrogen gas produced is collected over water. In the laboratory, the atmospheric pressure is 755 mmHg and the water temperature is 25°C. If the total volume of gas collected is 125 mL, what mass of zinc reacted?

 $Zn(s) + 2 HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$ 

# What happens when the KMT assumptions break down?

- 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
- 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

# Two major assumptions that break down

- Attractive forces
  - As particles become more massive, attractive forces increase
  - As pressure increases or when temperature decreases, particles get closer together and attractive forces increase
- Volume of particles
  - As particles become larger, their volume ceases to be negligible
  - When pressure increases or when temperature decreases, the fraction of the total volume that the particles occupy becomes less negligible
- Important indicators
  - High pressure
  - Low temperature
  - Mass/size of particles

## van der Waals equation: the next mathematical step in the KMT theory (a series expansion)

(V-nb)=nRTp + a

The actual pressure exerted by the gas is less than ideal because there are attractions that restrain the particles from causing pressure

$$P_{ideal} = P_{actual}$$

+ some amount that increases when density increases Reflects that the actual volume for particles to move in is smaller than the volume the gas occupies

b = volume occupied by
the particles
themselves (per mole)

# Which gases are more likely to deviate\* from ideal gas behavior? Why?

Assume all these gases are being compared at STP



#### Rank the degree of deviation of each gas from ideal behavior



## Key points so far

- 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

## Common phases of matter

- Particle level
  - How are these three phases different?
  - How does a material change from one phase to another? What happens at the particle level?
- Macroscopic behavior
  - How do these particle behaviors manifest in different macroscopic behavior?

# Three phases of matter: what do the particles do?

- Motion
- Proximity
- Density
- Interactions
- Timescale

Gas Total disorder; much empty space; particles have complete freedom of motion; particles far apart Liquid Disorder; particles or clusters of particles are free to move relative to each other; particles close together Copyright © 2006 Pearson Prentice Hall, Inc.



Crystalline solid Ordered arrangement; particles are essentially in fixed positions; particles close together

#### Show simulations of methane $(CH_4)$ gas.

Water behaves slightly differently due to  $H_2O$  to  $H_2O$  interactions being different than  $CH_4$  to  $CH_4$  interactions...we'll talk more about this next lecture (also in chapter 11).

Cool or compress

Heat or

reduce pressure

Particle level

### Change from one phase to another

- What kinds of energy are involved?
  - Kinetic energy = motion
  - Potential energy = separation
- How do particles get from one phase to another? Surfaces!
- Some vocabulary
  - Solid to liquid: melting
  - Liquid to solid: fusion (freezing)
  - Liquid to gas: vaporization (boiling)
  - Gas to liquid: condensation
  - Solid to gas: sublimation
  - Gas to solid: deposition



## Heating curve of water (1.00 mol at standard pressure)



#### Macroscopic

### Focus on Liquid to Gas: For a 1.00-mol sample of liquid water



ore heat

What happens if you add more heat energy to liquid water at 100°C and 1 atm?

It boils

Molecular dynamics simulation of water evaporating

- What is boiling?
  - There is a statistical range of kinetic energies (velocities) of particles in the liquid
  - Some particles will always have enough energy to break away from attractive forces that keep them in liquid → evaporation (vapor pressure)
  - As temperature rises, eventually it is high enough that so many particles can break away that their gas pressure (vapor pressure) equals the pressure of the surroundings → boiling
- Boiling continues with no change in temperature until all liquid particles have converted to gas phase
- Normal boiling point is temperature at which vapor pressure reaches atmospheric pressure when p<sub>atm</sub> = 1atm



# What we've learned about liquids and solids so far

- The same as in gases, there is a distribution of speeds of particles
- Both liquids and solids have *vapor pressure* at <u>every</u> temperature (even low temperatures)
- Vapor pressure is the pressure exerted by the gas particles that evaporate (L→G) or sublime (S→G) from a liquid or solid, respectively
- Evaporation and sublimation happen at the surface of the liquid or solid, where particles can escape from the surface
- When the vapor pressure reaches the pressure of whatever gas is surrounding the substance, we say that the substance is boiling (if it's changing from L→G) or subliming (S→G)