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
- 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: 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?

1. In a gas at a particular temperature, all of the particles move at the same speeds.
2. If two different gases are at the same temperature, they have the same distributions of particle speeds.
3. 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 III 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

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

Root mean square velocity

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

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

Does the equation make sense?

- What happens to average speed when temperature increases?  
  \[ v_{rms} = \sqrt{\frac{3RT}{M}} \]
- What happens to average speed when mass increases?
- How does the kinetic energy vary with temperature?
  \[ KE = \frac{1}{2} M v^2 = \frac{1}{2} M \frac{3RT}{M} = \frac{3}{2} RT \]
- Do the units make sense?
  \[ \text{Joules} = \left( \frac{kg}{s} \right)^2 = \frac{kg \cdot m^2}{s^2} \]

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
Last Thursday’s quandary

Question was: Why did the following happen?
- the SF₆ balloon got bigger
- the He balloon got smaller
- the N₂ and CO₂ balloons stayed about the same, though the CO₂ balloon was maybe a little bigger than the N₂ balloon

Explain what’s going on at the particle level and 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?
- [Link to animation](http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/gaslaw/effusion_macro.swf)
- This behavior is predicted by KMT

\[
\begin{align*}
T_A = T_B & \quad \text{so} \quad KE_A = KE_B \\
\text{and therefore,} \quad \frac{1}{2} m_A v_A^2 = \frac{1}{2} m_B v_B^2 & \\
\text{rearranging,} \quad \frac{v_A^2}{v_B^2} = \frac{m_B}{m_A} & \quad \text{or} \quad \frac{v_A}{v_B} = \sqrt{\frac{M_B}{M_A}} \\
\text{alternative:} \quad v_A = \sqrt{\frac{3RT}{M_A}} \quad \text{and} \quad v_B = \sqrt{\frac{3RT}{M_B}} \\
\text{therefore} \quad \frac{v_A}{v_B} = \sqrt{\frac{3RT}{M_B} \cdot \frac{M_B}{3RT \cdot M_A}} = \sqrt{\frac{M_B}{M_A}}
\end{align*}
\]

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).
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

\[
\frac{v_A}{v_B} = \sqrt{\frac{M_B}{M_A}}
\]

Compare what happened to the He and SF₆ 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 N₂ effuses in

- Which gases effused across the porous barrier?
- In what direction?
- Compare the rates of effusion
- Which gas effuses faster, SF₆ or N₂? How much faster?
What use is Graham’s law?

**Example:**
A sample of pure methane, CH₄, 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

\[ p_{total} = p_A + p_B + p_C + p_D + \ldots = \sum_i p_i \]
More about partial pressures

For a mixture with two gases (A and B):

\[
\begin{align*}
P_A + P_B &= \frac{p_{total}}{\frac{nRT}{V}} = \frac{n_A + n_B}{RT} \\
&= \frac{V}{(n_A + n_B)RT} \\
&= \frac{(n_A + n_B)RT}{V} \\
&= \frac{(n_A + n_B)p_{total}}{n_{total}} \\
&= \frac{n_A}{n_{total}}p_{total} + \frac{n_B}{n_{total}}p_{total} \\
&= P_A + P_B
\end{align*}
\]

Mole fractions:

\[
\chi_A = \frac{n_A}{n_{total}} \\
\chi_B = \frac{n_B}{n_{total}} \\
\chi_A + \chi_B = 1
\]

and generally, \( \sum \chi_i = 1 \)

Partial pressure definition:

\[
P_i = \chi_i p_{total}
\]

What use are partial pressures?

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

What gases are in here? What is the total pressure in here?

\[
p_{\text{atm, outside}}
\]

gas sample displacing water

gas producing reaction

\[
p_{\text{atm, inside}}
\]

water filled bottle

water bath

Total pressure inside must equal sum of partial pressures of water vapor and the gas being collected: \( p_{\text{atm}} = p_{\text{water}} + p_{\text{gas}} \)
Collecting a gas over water

*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?

\[
\text{Zn} \ (s) + 2 \text{HCl} \ (aq) \rightarrow \text{ZnCl}_2 \ (aq) + \text{H}_2 \ (g)
\]

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.

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
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
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)

\[
\left( p + a \frac{n^2}{V^2} \right) (V - nb) = nRT
\]

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

\[ P_{\text{ideal}} = P_{\text{actual}} + \text{some amount that increases when density increases} \]

Reflects that the actual volume for particles to move in is smaller than the volume the gas occupies

\[ b = \text{volume occupied by the particles themselves (per mole)} \]
Which gases are more likely to deviate* from ideal gas behavior? Why?

Assume all these gases are being compared at STP

- H₂
- O₂
- H₂O
- Xe
- C₄H₁₀
- He
- Ne

*to deviate = to be different from

- 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

Rank the degree of deviation of each gas from ideal behavior

<table>
<thead>
<tr>
<th>Completely ideal behavior</th>
<th>Increasing deviations from ideal behavior</th>
<th>Very non-ideal behavior</th>
</tr>
</thead>
</table>

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Key points so far

- \( pV/nT = \text{constant} \)
- \( pV = nRT \) (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

Show simulations of methane (CH₄) gas.
Water behaves slightly differently due to H₂O to H₂O interactions being different than CH₄ to CH₄ interactions…we’ll talk more about this next lecture (also in chapter 11).

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 1.00-gram Sample of Methane (CH₄) at Standard Pressure

<table>
<thead>
<tr>
<th>Temperature (Celsius)</th>
<th>Energy added (Joules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>A = solid below melting*</td>
</tr>
<tr>
<td>20</td>
<td>B = solid has reached melting temperature, and is beginning to melt*</td>
</tr>
<tr>
<td>40</td>
<td>C = liquid at melting temperature, has just completed melting</td>
</tr>
<tr>
<td>60</td>
<td>D = liquid has reached boiling temperature, and is beginning to boil*</td>
</tr>
<tr>
<td>80</td>
<td>E = gas at boiling temperature, has just completed boiling*</td>
</tr>
<tr>
<td>100</td>
<td>F = gas above boiling temperature</td>
</tr>
</tbody>
</table>

No numbers shown for Joules. The point is to note the form of the graph.

See [http://www.chemistry.wustl.edu/~gelb/gchem/materials/phases/](http://www.chemistry.wustl.edu/~gelb/gchem/materials/phases/)

Heating curve of water
(1.00 mol at standard pressure)
Focus on Liquid to Gas:
For a 1.00-mol sample of liquid water

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

- It boils
- 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 $P_{atm} = 1$ atm
Comparing a liquid at two temperatures

The effect of temperature on the distribution of kinetic energies in a liquid

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 every temperature (even low temperatures)
- Vapor pressure is the pressure exerted by the gas particles that evaporate (L$\rightarrow$G) or sublime (S$\rightarrow$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$\rightarrow$G) or subliming (S$\rightarrow$G)