Chemistry 1314 – Lecture Outline and Notes
Text: Chemistry – The Central Science, 10th edition, Brown, LeMay and Bursten

Chapter 10. Gases

Gases are the most easily understood form of matter. There are many different types with different chemical properties, but they all have very similar physical properties.

Characteristics of gases

- Gases are highly compressible and occupy the full volume of their containers.
- When a gas is subjected to pressure, its volume decreases.
- Gases always form homogeneous mixtures with other gases.
- Gases only occupy about 0.1% of the volume of their containers.

Pressure

- Pressure is the force acting on an object per unit area: P = F/A
    - P = pressure, F = force, A = area
    - Force is mass x acceleration: F = ma
- Gravity (an acceleration) exerts a pressure on the earth's atmosphere
- A column of air 1 m^2 in cross section has a mass of about 10,000 kg and exerts a force of 10^5 N.
- The pressure of a 1 m^2 column of air is 100 kPa. Pa is Pascal
- SI Units: 1 N = 1 kg·m/s^2; 1 Pa = 1 N/m^2. N is Newton.
- You will also see bar = 10^5 Pa
- Atmospheric pressure is measured with a barometer.
- If a tube is inserted into a container of mercury open to the atmosphere, the mercury will rise 760 mm up the tube.
- Standard atmospheric pressure is the pressure required to support 760 mm of Hg in a column.
- **Units: 1 atm = 760 mmHg = 760 torr = 1.01325 × 10^5 Pa = 101.325 kPa.**
- The pressures of gases not open to the atmosphere are measured in manometers.
- A manometer consists of a bulb of gas attached to a U-tube containing Hg:

- If $P_{gas} < P_{atm}$ then $P_{gas} + P_h = P_{atm}$.
- If $P_{gas} > P_{atm}$ then $P_{gas} = P_{atm} + P_h$.

The Gas Laws

The pressure-volume relationship: Boyle's Law

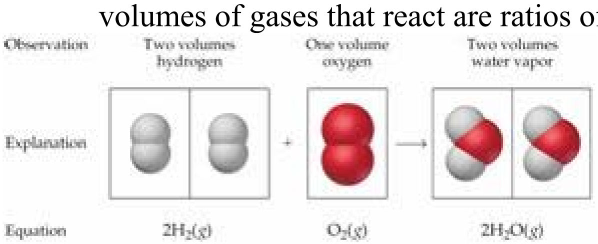
- If the pressure on a balloon is decreased (such as when it rises through the atmosphere) the balloon expands.
- If the pressure is increased, the volume of the gas is compressed.
- Boyle's Law: the volume of a fixed quantity of gas is inversely proportional to its pressure.
- Mathmatically:
    - V = constant x 1/P or PV = constant

The temperature-volume relationship: Charle's Law

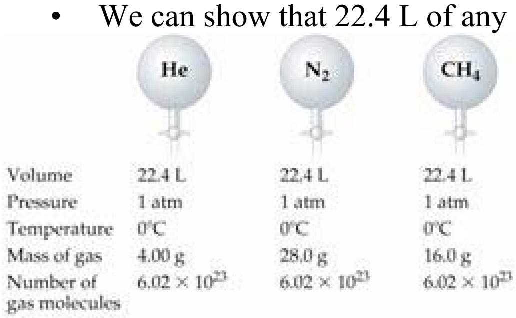
- We know that hot-air balloons expand when they are heated.
- Charles's Law: the volume of a fixed quantity of gas at constant pressure increases as the temperature increases.
- Mathematically:
    - V = constant x T or V/T = constant
- A plot of V versus T is a straight line.
- When T is measured in °C, the intercept on the temperature axis is -273.15°C.
- We define absolute zero, 0 K = -273.15°C.
- At this point, the volume is zero; but this is not obtained because gases liquefy or solidify before obtaining this temperature.

The quantity-volume relationship: Avogadro's Law

- As we add gas to a balloon, it expands. The volume is affected by the amount of gas.
- Gay-Lussac's Law of combining volumes: at a given temperature and pressure, the volumes of gases that react are ratios of small whole numbers.



- Avogadro's Hypothesis: equal volumes of gas at the same temperature and pressure will contain the same number of molecules.
- Avogadro's Law: the volume of gas at a given temperature and pressure is directly proportional to the number of moles of gas.
- Mathematically:
    - V = constant x n
- We can show that 22.4 L of any gas at 0°C and 1 atm contain 6.02×10^{23} gas molecules.



The Ideal-Gas Equation

- Consider the three gas laws.
  - Boyle's Law: $V \propto 1/P$ (at constant n and T)
  - Charles' Law: $V \propto T$ (at constant n and P)
  - Avogadro's Law: $V \propto n$ (at constant P and T)
- We can combine these into a general gas law:

  $V \propto (nT/P)$
- If *R* is the constant of proportionality (called the **gas constant**), then

  $V = R(nT/P)$
- The **ideal gas equation** is:

  $PV = nRT$
- R = 0.08206 L·atm/mol·K = 8.314 J/mol·K
- We define STP (standard temperature and pressure) = 0°C or 273.15 K, 1 atm.
- Volume of 1 mol of gas at STP is:

  $PV = nRT$

  V = nRT/P = (1.000 mol)(0.08206 L-atm/mol-K)(273.15 K)/ 1.000 atm

  V = 22.41 L, which is the *molar volume* of a gas at STP.

Example: Tennis balls are usually filled with air or N_2 gas to a pressure above atmospheric pressure to increase their "bounce". If a particular tennis ball has a volume of 144 cm^3 and contains 0.33 g of N_2 gas, what is the pressure inside the ball at 24°C?

Relating the ideal-gas equation and the gas laws

- If $PV = nRT$ and n and T are constant, then PV = constant and we have Boyle's law.
- Other laws can be generated similarly.
- In general, if we have a gas under two sets of conditions, then

  $P_1V_1/n_1T_1 = P_2V_2/n_2T_2$

Example: A large natural-gas storage tank is arranged so that the pressure is maintained at 2.20 atm. On a cold day in December when the temperature is -15°C (4°F), the volume of gas in the tank is 28,500 ft^3. What is the volume of the same quantity of gas on a warm July day when the temperature is 31°C (88°F)?

Further Applications of the Ideal-Gas Equation

Gas densities and molar mass

- Density has units of mass over volume. For a gas usually g/L
- Rearranging the ideal-gas equation with *MM* as molar mass we get
  - $PV = nRT$
  - $n/V = P/RT$
    - Notice that n/V has units of mol/L. If we multiply both sides by the molar mass, *MM* (the number of grams of a substance in 1 mol of substance, AKA the molecular weight) we get:
    - $nMM/V = PMM/RT$
    - The product of nMM/V is in g/L, this equals the density, *d*
    - Therefore $d = PMM/RT$

Example: The mean molar mass of the atmosphere at the surface of Titan, Saturn's largest moon, is 28.6 g/mol. The surface temperature is 95 K, and the pressure is 1.6 atm. Assuming ideal behavior, calculate the density of Titan's atmosphere.

- The molar mass of a gas can be determined as follows:

  $MM = dRT/P$

Example: Calculate the average molar mass of dry air if it has a density of 1.17 g/L at 21°C and 740.0 torr.

Volumes of gases in chemical reactions

- The ideal-gas equation relates *P*, *V*, and *T* to number of moles of gas.
- The *n* can then be used in stoichiometric calculations.

Example: In the first step in the industrial process for making nitric acid, ammonia reacts with oxygen in the presence of a suitable catalyst to form nitric oxide and water vapor:

$4NH_3\ (g) + 5O_2\ (g) \rightarrow 4NO\ (g) + 6H_2O\ (g)$

How many liters of NH_3 (g) at 850°C and 5.00 atm are required to react with 1.00 mol of O_2 (g) in this reaction?

Gas Mixtures and Partial Pressures

- So far, we have only looked at the behavior of pure gases, how do we deal with a mixture of 2 or more different gases?
- Since gas molecules are so far apart, we can assume they behave independently.
- Dalton's Law: in a gas mixture the total pressure is given by the sum of partial pressures of each component:

  $P_t = P_1 + P_2 + P_3 + \ldots$

- Each gas obeys the ideal gas equation:

  $P_i = n_i[RT/V]$

- Combing the equations

  $P_t = (n_1 + n_2 + n_3 + \quad)(RT/V) = n_t(RT/V)$

Example: What is the total pressure exerted by a mixture of 2.00 g of H_2 and 8.00 g of N_2 at 273 K in a 10.0 L vessel?

Partial pressures and mole fractions

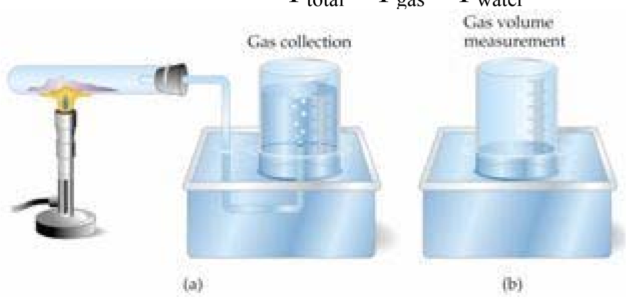
Let n_i be the number of moles of gas i exerting a partial pressure P_i, then

$P_i = X_iP_t$; where X_i is the mole fraction (n_i/n_t)

Collecting gases over water

- It is common to synthesize gases and collect them by displacing a volume of water.
- To calculate the amount of gas produced, we need to correct for the partial pressure of the water:

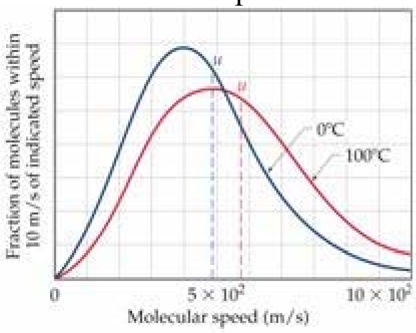
  $P_{total} = P_{gas} + P_{water}$



Kinetic-Molecular Theory

- Theory developed to explain gas behavior.
- Theory of moving molecules.
- Assumptions:
  - Gases consist of a large number of molecules in constant random motion.
  - Volume of individual molecules negligible compared to volume of container.
  - Intermolecular forces (forces between gas molecules) negligible.
  - Energy can be transferred between molecules, but total kinetic energy is constant at constant temperature.
  - Average kinetic energy of molecules is proportional to temperature.
- Kinetic molecular theory gives us an understanding of pressure and temperature on the molecular level.
- Pressure of a gas results from the number of collisions per unit time on the walls of container.
- Magnitude of pressure given by how often and how hard the molecules strike.

- Gas molecules have an average kinetic energy.
- Each molecule has a different energy.
- There is a spread of individual energies of gas molecules in any sample of gas.
- As the temperature increases, the average kinetic energy of the gas molecules increases.



- As kinetic energy increases, the velocity of the gas molecules increases.
- Root mean square (rms) speed, u, is the speed of a gas molecule having average kinetic energy.
- Average kinetic energy, ε, is related to root mean square speed: $\varepsilon = \frac{1}{2}mu^2$

Application to gas law

- As volume increases at constant temperature, the average kinetic energy of the gas remains constant. Therefore, u is constant. However, volume increases so the gas molecules have to travel further to hit the walls of the container. Therefore, pressure decreases.
- If temperature increases at constant volume, the average kinetic energy of the gas molecules increases. Therefore, there are more collisions with the container walls and the pressure increases.

Molecular Effusion and Diffusion

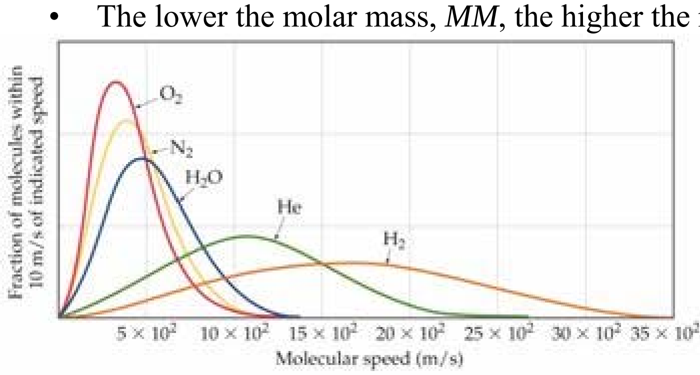
- As kinetic energy increases, the velocity of the gas molecules increases.
- Average kinetic energy of a gas is related to its mass:

$$\varepsilon = \frac{1}{2}mu^2$$

- Consider two gases at the same temperature: the lighter gas has a higher rms speed than the heavier gas.
- Mathematically:

$$u = \sqrt{\frac{3RT}{MM}}$$

- The lower the molar mass, MM, the higher the rms speed.



Graham's law of effusion

- As kinetic energy increases, the velocity of the gas molecules increases.
- Effusion is the escape of a gas through a tiny hole (a balloon will deflate over time due to effusion).
- The rate of effusion can be quantified.
- Consider two gases with molar masses MM_1 and MM_2, the relative rate of effusion is given by:

$$\frac{r_1}{r_2} = \sqrt{\frac{MM_2}{MM_1}}$$

- Only those molecules that hit the small hole will escape through it.
- Therefore, the higher the rms the more likelihood of a gas molecule hitting the hole.

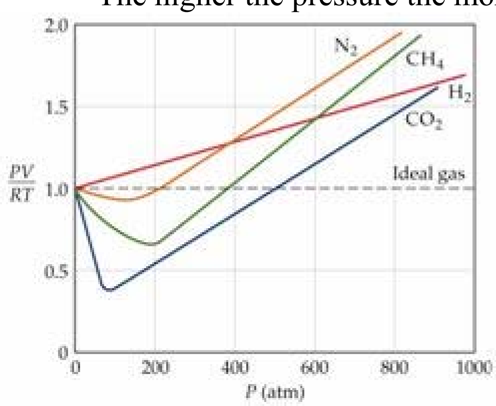
Diffusion and mean free path

- Diffusion of a gas is the spread of the gas through space.
- Diffusion is faster for light gas molecules.
- Diffusion is significantly slower than rms speed (consider someone opening a perfume bottle: it takes a while to detect the odor but rms speed at 25°C is about 1150 mi/hr).
- Diffusion is slowed by gas molecules colliding with each other.
- Average distance of a gas molecule between collisions is called mean free path.
- At sea level, mean free path is about 6×10^{-6} cm.

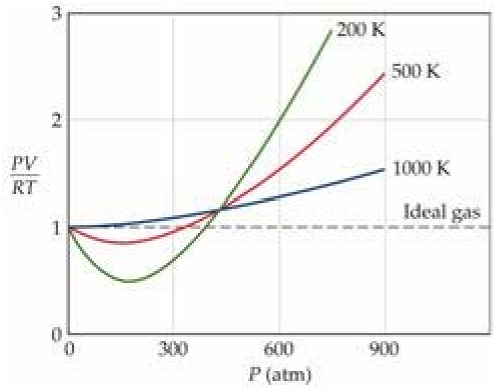
<u>Real Gases: Deviations from Ideal Behavior</u>

- From the ideal gas equation, we have

  PV/RT = n
- For 1 mol of gas, $PV/RT = 1$ for all pressures.
- In a real gas, PV/RT varies from 1 significantly.
- The higher the pressure the more the deviation from ideal behavior.



- For 1 mol of gas, $PV/RT = 1$ for all temperatures.
- As temperature increases, the gases behave more ideally.
- The assumptions in kinetic molecular theory show where ideal gas behavior breaks down:
  - the molecules of a gas have finite volume;
  - molecules of a gas do attract each other.



- As the pressure on a gas increases, the molecules are forced closer together.
- As the molecules get closer together, the volume of the container gets smaller.
- The smaller the container, the more space the gas molecules begin to occupy.
- Therefore, the higher the pressure, the less the gas resembles an ideal gas.
- As the gas molecules get closer together, the smaller the intermolecular distance.
- The smaller the distance between gas molecules, the more likely attractive forces will develop between the molecules.
- Therefore, the less the gas resembles an ideal gas.
- As temperature increases, the gas molecules move faster and further apart.
- Also, higher temperatures mean more energy available to break intermolecular forces.
- Therefore, the higher the temperature, the more ideal the gas.

The van der Waals Equation

- We add two terms to the ideal gas equation one to correct for volume of molecules and the other to correct for intermolecular attractions
- The correction terms generate the van der Waals equation:

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

where a and b are empirical constants. nb is a correction for volume of molecules and n^2a/V^2 is a correction for molecular attraction.