Lecture Notes: Gas Laws and Kinetic Molecular Theory (KMT).

Gases

- Are mostly empty space
- Occupy containers uniformly and completely
- Expand infinitely
- Diffuse and mix rapidly

Because gases are mostly empty space, they are used to fill airbags to cushion the shock from an impact. The chemical reaction that fills an airbag is from the decomposition of sodium azide (NaN_3):

$NaN_3(s) \rightarrow Na(s) + 3N_2(g)$

Mathematical models explain the behavior of gases. The models include one or more of these quantities:

P = pressure (in units of atmospheres)
V = volume of the gas (in units of L)
T = temperature (in units of K)
n = amount (in units of mole)
R = gas constant 0.0821 (L*atm)/(mol*K)

Barometers measure pressure. Barometers may measure in pressure units other than atmospheres (atm). The SI unit for pressure is the Pascal (Pa). The conversions among various pressure units are:

1 atm = 760 mm Hg column = 29.9 inches Hg = about 34 feet of water = 101.325 kPa

To get temperature in Kelvin, add 273 to the Celsius temperature.

The Ideal Gas Law, PV = nRT, models the behavior of ideal gases. Other gas laws can be derived from the Ideal Gas Law for either one set of conditions or for two sets of conditions (initial and final conditions).

To derive gas laws for two sets of conditions, solve the Ideal Gas Law for R

$$\frac{PV}{nT} = R$$

If the Ideal Gas Law is correct, the above would apply under any set of conditions of P, V, n, and T, giving (where 1 represents the initial conditions and 2 represents the final conditions):

Equation 1. Ideal Gas Law for two sets of conditions.

$$\frac{P_1V_1}{n_1T_1} = R = \frac{P_2V_2}{n_2T_2}$$

Boyle's Law says that when n and T are constant, the following equations apply:

One set of conditions	Two sets of conditions
$PV = k = nRT$	$P_1V_1 = P_2V_2$
Pressure times volume equals a constant value	When n_1=n_2 and T_1=T_2 these quantities algebraically cancel from Equation 1.

Example: Calculate the final pressure when a system with an initial pressure of 1.0atm and an initial volume was 2.0L was expanded to a volume of 4.0L.

Solution: Because temperature and moles are not mentioned in the problem, one must presume that the system was closed (no change in moles), and that there was no change in temperature between the initial and final conditions. (If this was not true, than there is no possible solution using the Ideal Gas Law.) Using n and T as constant gives P_1V_1 = P_2V_2; (1atm)(2.0L) = P_2(4.0L), and P_2 = 0.50atm.

Boyle's Law says that as pressure increase, the volume decreases (an inverse relationship), doubling the pressure halves the volume. For example, pushing down on a sealed gas-filled syringe would increase the pressure inside the syringe.

Charles's Law says that when n and P are constant, the following equations apply:

One set of conditions	Two sets of conditions
$V/T = k = nR/P$	$V_1/T_1 = V_2/T_2$
Volume divided by temperature equals a constant value	When n_1=n_2 and P_1=P_2 these quantities algebraically cancel from Equation 1.

Charles's Law says that as the volume increases, the temperature increases (a direct relationship), doubling the volume doubles the pressure. For example, putting a balloon filled at room temperature into a hot car would cause the balloon to expand (and possibly pop), so put the air conditioner on in the car first.

Charles's Law can be used to approximate absolute zero. At a temperature of absolute zero (0K), theoretically an ideal gas has no volume. Experimentally, scientists have reached within nanokelvins of absolute zero, and gases still have volume.

Avogadro's Law says that when T and P are constant, the following equations apply:

One set of conditions	Two sets of conditions
$V/n = k = RT/P$	$V_1/n_1 = V_2/n_2$
Volume divided by temperature equals a constant value	When $T_1=T_2$ and $P_1=P_2$ these quantities algebraically cancel from Equation 1.

Avogadro's Law says that as the number of moles of gas increases, the volume increases, (a direct relationship), doubling the number of moles of gas doubles the volume of gas. For example, adding twice the number of moles of gas to a balloon would double the balloon's volume.

Avogadro's Law can be used to predict the volume(s) of reactant(s) before a chemical reaction or volume(s) of product(s) after a chemical reaction. The connection between gas laws and chemistry is through the mole (n). The equation below reacts 8 moles of hydrogen gas with 4 moles of oxygen gas to produce 8 moles of water gas.

	$2H_2(g)$	+	$O_2(g)$	$\rightarrow$	$2H_2O(g)$
mol	8	+	4	$\rightarrow$	8
V, L	8	+	4	$\rightarrow$	8

If 8 moles of $H_2(g)$ has a volume of 8L under a set of conditions (the proportionality constant, k, equals 1), then 4 moles of $H_2(g)$ would have a volume of 4L. Also, 4 moles of $O_2(g)$ (or any other ideal gas) would have a volume of 4L under those conditions. The reactants together (H_2 and O_2) then represent 12 moles and combined volume of 12L. The product, 8 moles of $H_2O(g)$, occupies a volume of 8L. Avogadro's Law says that the volume of an ideal gas increases in direct proportion to the number of moles of gas at constant pressure and temperature.

Standard temperature and pressure (STP) for gas laws is 273K (0°C) and 1atm pressure (760 mmHg). If a gas law problem mentions STP, that means the conditions are T=273K and P=1atm.

Using the Ideal Gas Law

Example: Calculate the standard volume for 1 mole of gas at STP.

Solution: Plug the conditions of STP (T=273K, P=1atm) into the Ideal Gas Law (PV = nRT) and solve for volume.
(1atm)(V) = (1mol)(0.0821L atm/mol K)(273K)
V = 22.4L, so the standard volume is 22.4L, which means that 1mol of an ideal gas at STP has a volume of 22.4L.

Example: Calculate the amount (mol) of ideal gas required to fill a room that measures 10.0m by 10.0m by 8.0m at 725mmHg and 37°C.

Solution: To use the gas constant, R=0.0821, with units of L atm/mol K, convert the given quantities to the units of R (Note: this value of R is given on the page of conversion factors and constants that appears on the exam), then use the Ideal Gas Law to calculate moles.
The pressure in atmospheres is 725mmHg (1atm/760mmHg) = 0.954atm.
The temperature in Kelvin is 37°C + 273 = 310K.
The volume of the room is (10.0m)(10.0m)(8.0m)=800m^3. To convert this to liters, you can use 1L=1dm^3, or 1mL=1cm^3. This gives V=800m^3(1dm/0.1m)^3(1L/1dm^3) = 800,000L.
Calculate the number of moles using PV=nRT. This gives (0.954atm)(800,000L) = n (0.0821L atm/mol K)(310K), or n= 30,000mol. If nitrogen gas fills the room, then the molar mass of nitrogen can be used to calculate the mass of gas in the room: 30,000mol N_2 (28.014g N_2/mol N_2) = 840,000g N_2.

Apply gas laws only to substances that are gases. For example, warm water at 48°C and 1atm pressure is cooled to 25°C. Do not apply gas laws in an attempt to calculate the pressure above the cool water because water is a liquid, not a gas.

Gas Laws and Stoichiometry

Example: 5.5g of sodium carbonate decomposes to sodium oxide and carbon dioxide in a sealed 5.0L flask. What is the pressure inside the flask after the reaction goes to completion and the temperature is 25°C?

Solution: Write the balanced chemical reaction. Calculate the number of moles of gas produced. Determine the pressure of gas in the flask using the Ideal Gas Law. To start the problem, calculate the molar mass of sodium carbonate (105.988g/mol).

Balanced chemical reaction

	$Na_2CO_3(s) \rightarrow$	$Na_2O(s) +$	$CO_2(g)$
g	5.5		
	| Step 1		
mol	0.0519	—	0.0519
		Step2	

Moles of gas produced

5.5g Na_2CO_3 (1mol Na_2CO_3/105.988g Na_2CO_3)(1mol CO_2/1mol Na_2CO_3) = 0.0519mol CO_2.

Pressure in flask

P(5.0L) = (0.0519mol)(0.0821L atm/mol K)(298K)

P= 0.254atm.

Dalton's Law of Partial Pressures says that the total pressure from a mixture of gases is the sum of the partial pressures of the individual gases that make up the mixture.

$P_T = P_A + P_B + P_C + \ldots$

Example: What would be the total pressure in the 5.0L flask in the previous example if it initially contained a pressure of 1.256atm of N_2 gas?

Solution: Pressures are additive. Apply Dalton's Law of Partial Pressures the total pressure of gas by adding the partial pressures from each gas in the mixture. $P_T = P_{O2} + P_{N2}$ = 1.256atm + 0.254atm = 1.510atm.

The **density of a gas** is proportional to its molar mass. As the molar mass of a gas increases, so does the density of the gas. Matter often separates according to its density, with less dense matter floating on matter of higher density. Hydrogen and helium, gases that have lower molar masses than air, are less dense than air and float on air. Helium balloons float.

The relationship between molar mass and density of gas comes by substituting into the Ideal Gas Law: PV = nRT. The molar mass of substance (M) is given by the mass of a substance (m) divided by the number of moles of substance (n): M=m/n. Solving for n gives n=m/M. Replacing n in the Ideal Gas Law with m/M gives: PV = (m/M)RT. Density of a substance is given by mass (m) over volume (V). Solving the previous expression for m/V gives d= m/V= PM/RT. The equation says that density of a gas increases with increasing molar mass and pressure, and decreases with increasing temperature (when other quantities are held constant).

Kinetic Molecular Theory (KMT) explains the gas laws from a theoretical standpoint. The assumptions for KMT are:
1) Gases consist of molecules in constant, random motion.
2) Pressure arises from collisions with container walls.
3) No attractive or repulsive forces between molecules. Collisions are elastic.
4) Volume of molecules is negligible.
Assumptions 1 and 2 are reasonably good. Assumptions 3 and 4 cause the Ideal Gas Law to fail at high pressures, high numbers of moles, low temperatures, and low volumes, as will be explained later.

Molecules in motion have a kinetic energy (KE) that is given by the mass (m) times the speed (V) squared: KE= ½ mV^2. At the same temperature, all gases have the same average kinetic energy. Maxwell's equation gives the relationship between root-mean-square speed, temperature (T), and molar mass (M) as:

$$\sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{M}}$$

Maxwell's equation tells us that the root-mean-square speed increases with increasing temperature and decreases with increasing molar mass. Because speed increases with increasing temperature as given by Maxwell's equation, kinetic energy also increases with increasing temperature.

Effusion is the movement of gas molecules through a tiny hole into an empty container. Gases can escape a balloon by effusion, and the rate of effusion increases with increasing temperature and decreasing molar mass because gas molecules move faster with higher temperatures and lower mass. The rates of effusion for two gases are given by the following equation:

$$\frac{Rate\_Of\_Effusion\_A}{Rate\_Of\_Effusion\_B} = \sqrt{\frac{M_B}{M_A}}$$

According to KMT, pressure is proportional to number of moles of gas (with fixed T and V) because the number of collisions with the container walls doubles as the number of moles of gas doubles, therefore, the pressure doubles.

According to KMT, pressure is proportional to temperature (with fixed V and n) because the average speed of gas increases with increasing temperature. Collisions with container walls occur more often; therefore, the pressure increases.

According to KMT, pressure is inversely proportional to volume (with fixed T and n) because as the volume of the container increases, collisions with the wall occur less often. This results in a drop in pressure.

Real gases deviate from ideal behavior because real gases have intermolecular forces and real gases have volume. If there were no intermolecular forces, gases could not be made into liquids and solids because they would not stick together. Conditions of low temperature, low volume, high number of moles, and high pressure puts molecules close together, which makes the factors of intermolecular forces and gas volume to become important.

The Van der Waals equation models the behavior of gases when deviations from the Ideal Gas Law occur because the equation accounts for the volume of gas (nb) and intermolecular forces (n^2a/V). The Van der Waals equation is:

$$(P + n^2a/V)\ (V - nb) = nRT$$

The measured pressure, P, gets increased by the term, n^2a/V, that accounts for the pressure drop from intermolecular forces. The measured volume gets decreased by the volume occupied by the gas, nb.

The pressure predicted by Van der Waals equation is generally lower than that predicted by the Ideal Gas Law because intermolecular forces cause molecules to stick together, making collisions with container walls occur less often.