AP* Chemistry
GASES

THE PROPERTIES OF GASES

Only 4 quantities are needed to define the **state of a gas**:

a) the *quantity* of the gas, n (in moles)
b) the *temperature* of the gas, T (**in KELVINS)**
c) the *volume* of the gas, V (in liters)
d) the *pressure* of the gas, P (in atmospheres)

A gas uniformly fills any container, is easily compressed & mixes completely with any other gas.

GAS PRESSURE:

A measure of the force that a gas exerts on its container. Force is the physical quantity that interferes with inertia. Gravity is the force responsible for weight.

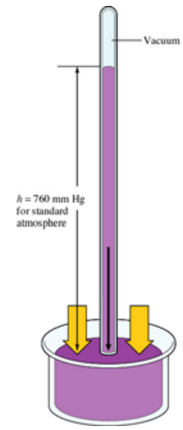
Force = mass × acceleration; Newton's 2nd Law. The units of force follow:

$\text{N} = \text{kg} \times \text{m/s}^2$

Pressure-- Force/ unit area; N/m^2

Barometer--invented by Evangelista Torricelli in 1643; uses the height of a column of mercury to measure gas pressure (especially atmospheric)

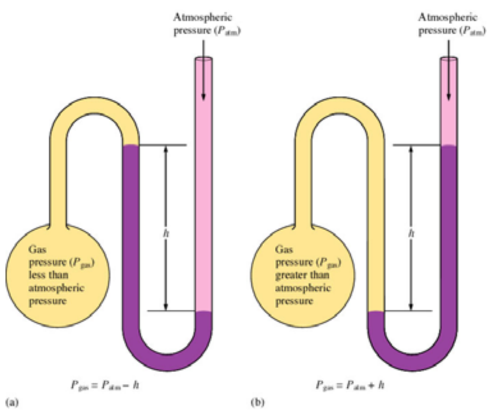
1 mm of Hg = 1 torr



Early barometer

760.00 mm Hg = 760.00 torr =1.00 atm = 101.325 kPa $\approx 10^5$ Pa

At sea level all of the above define STANDARD PRESSURE. The SI unit of pressure is the Pascal (Blaise Pascal); $1 \text{ Pa} = 1 \text{ N / m}^2$



The **manometer**—a device for measuring the pressure of a gas in a container. The pressure of the gas is given by h [the difference in mercury levels] in units of torr (equivalent to mm Hg).

a) Gas pressure = atmospheric pressure – h

b) Gas pressure = atmospheric pressure + h

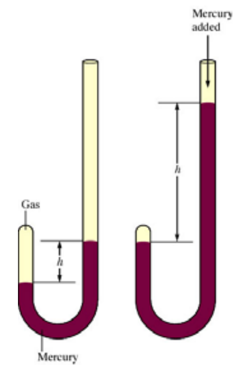
Exercise 1 Pressure Conversions

The pressure of a gas is measured as 49 torr. Represent this pressure in both atmospheres and pascals.

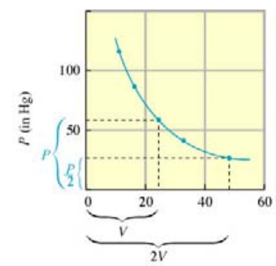
6.4×10^{-2} atm
6.5×10^3 Pa

Exercise
Rank the following pressures in decreasing order of magnitude (largest first, smallest last): 75 kPa, 300. torr, 0.60 atm and 350. mm Hg.

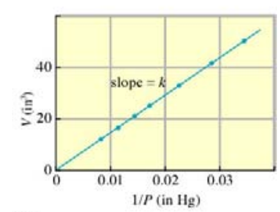
GAS LAWS: THE EXPERIMENTAL BASIS



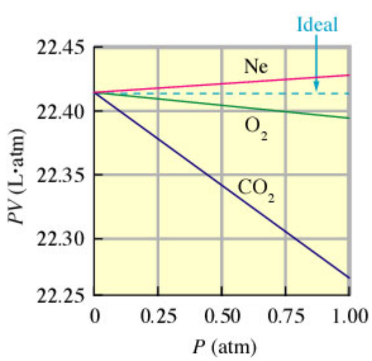
- BOYLE'S LAW: "father of chemistry"--*the volume of a confined gas is inversely proportional to the pressure exerted on the gas.* ALL GASES BEHAVE IN THIS MANNER!
- Robert Boyle was an Irish chemist. He studied *PV* relationships using a J-tube set up in the multi-story entryway of his home.
  - o $P \propto 1/V$ plot = straight line
  - o pressure and volume are **inversely** proportional
  - o Volume ↑ pressure ↓ **at constant temperature,** the converse is also true
  - o *for a given quantity of a gas at constant temperature, the product of pressure and volume is a constant.*
    - ▪ $PV = k$
    - ▪ Therefore, $V = \frac{k}{P} = k\frac{1}{P}$
    - ▪ which is the equation for a straight line of the type
    - ▪ $y = mx + b$ where m = slope, and b the y-intercept
    - ▪ In this case, $y = V$, $x = 1/P$ and $b = 0$. Check out the plot on the right (b). The data Boyle collected is graphed on (a) above.
  - o $P_1V_1 = P_2V_2$ is the easiest form of Boyle's law to **memorize**
  - o Boyle's Law has been tested for over three centuries. It holds true ***<u>only at low pressures</u>***.



(a)



(b)



A plot of *PV* versus P for several gases at pressures below 1atm is pictured at left.

An **ideal** gas is expected to have a constant value of *PV*, as shown by the dotted line. CO_2 shows the largest change in PV, and this change is actually quite small: *PV* changes from about 22.39 L·atm at 0.25 atm to 22.26 L·atm at 1.00 atm. Thus Boyle's Law is a good approximation at these relatively low pressures.

Exercise 2 **Boyle's Law I**

Sulfur dioxide (SO_2), a gas that plays a central role in the formation of acid rain, is found in the exhaust of automobiles and power plants. Consider a 1.53- L sample of gaseous SO_2 at a pressure of 5.6×10^3 Pa. If the pressure is changed to 1.5×10^4 Pa at a constant temperature, what will be the new volume of the gas ?

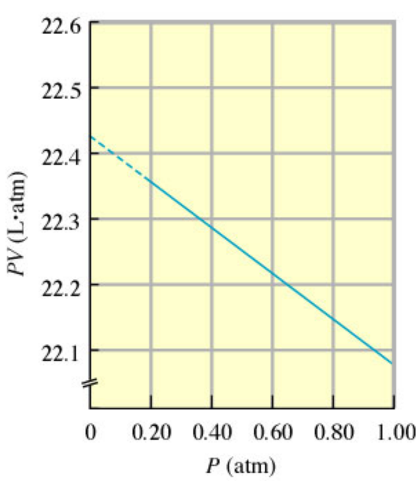
0.57 L

Exercise 3 **Boyle's Law II**

In a study to see how closely gaseous ammonia obeys Boyle's law, several volume measurements were made at various pressures, using 1.0 mol NH_3 gas at a temperature of 0ºC. Using the results listed below, calculate the Boyle's law constant for NH_3 at the various pressures.

Experiment	*Pressure (atm)*	*Volume (L)*
1	0.1300	172.1
2	0.2500	89.28
3	0.3000	74.35
4	0.5000	44.49
5	0.7500	29.55
6	1.000	22.08

experiment 1 is 22.37
experiment 2 is 22.32
experiment 3 is 22.31
experiment 4 is 22.25
experiment 5 is 22.16
experiment 6 is 22.08



PLOT the values of *PV* for the six experiments above.

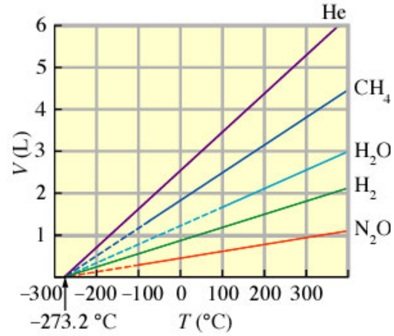
Extrapolate it back to see what PV equals at 0.00 atm pressure.

Compare it to the *PV* vs. *P* graph on page 2 of these notes.

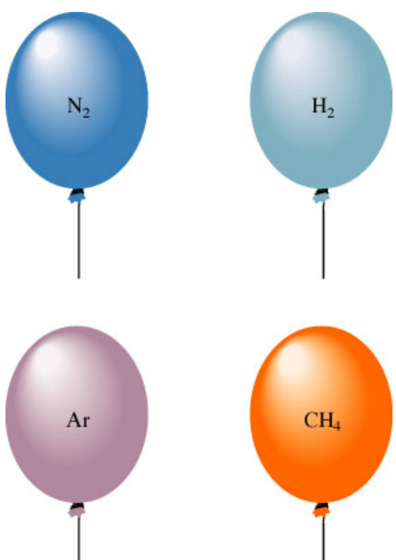
What is the *y*-intercept for all of these gases?

Remember, gases behave most ideally at low pressures. You can't get a pressure lower than 0.00 atm!

- **CHARLES= LAW**: *If a given quantity of gas is held at a constant pressure, then its volume is directly proportional to the absolute temperature.* **Must use KELVIN**
- Jacques Charles was a French physicist and the first person to fill a hot “air” balloon with hydrogen gas and made the first solo balloon flight!
  - o $V \propto T$ plot = straight line
  - o $V_1T_2 = V_2T_1$
  - o Temperature 8 Volume 8 **at constant pressure**
  - o This figure shows the plots of *V* vs. *T* (Celsius) for several gases. The solid lines represent experimental measurements on gases. The dashed lines represent extrapolation of the data into regions where these gases would become liquids or solids. Note that the samples of the various gases contain different numbers of moles.
  - o What is the temperature when the Volume extrapolates to zero?



Exercise 4	**Charles’s Law**
A sample of gas at 15ºC and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38ºC and 1 atm ?	
	2.79 L



These balloons each hold 1.0 L of gas at 25°C and 1 atm. Each balloon contains 0.041 mol of gas, or 2.5×10^{22} molecules.

- **GAY-LUSSAC’S LAW of combining volumes:** volumes of gases always combine with one another in the ratio of small whole numbers, as long as volumes are measured at the same *T* and *P*.
  - $P_1T_2 = P_2T_1$
  - Avogadro=s hypothesis: *equal volumes of gases under the same conditions of temperature and pressure contain equal numbers of molecules.*
- **AVOGADRO’S LAW:** *The volume of a gas, at a given temperature and pressure, is directly proportional to the quantity of gas.*
  - $V \propto n$
  - $n \propto$ Volume **at constant T & P**

HERE’S AN EASY WAY TO MEMORIZE ALL OF THIS!
Start with the combined gas law:

$$P_1V_1T_2 = P_2V_2T_1$$ Memorize it.

Next, put the fellas’ names in alphabetical order.
Boyle’s uses the first 2 variables, Charles’ the second 2 variables & Gay-Lussac’s the remaining combination of variables. What ever doesn’t appear in the formula, is being held CONSTANT!

Exercise 5 **Avogadro's Law**

Suppose we have a 12.2-L sample containing 0.50 mol oxygen gas (O_2) at a pressure of 1 atm and a temperature of 25ºC. If all this O_2 were converted to ozone (O_3) at the same temperature and pressure, what would be the volume of the ozone ?

8.1 L

THE IDEAL GAS LAW

Four quantities describe the state of a gas: pressure, volume, temperature, and # of moles (quantity). Combine all 3 laws:

$$V \propto \frac{nT}{P}$$

Replace the $\propto$ with a constant, R, and you get:

$$PV = nRT$$

The ideal gas law! ***It is an equation of state***.

R = 0.08206 L• atm/mol • K also expressed as 0.08206 L atm mol^{-1} K^{-1}

Useful only at low Pressures and high temperatures! Guaranteed points on the AP Exam!

These next exercises can all be solved with the ideal gas law, BUT, you can use another if you like!

Exercise 6 **Ideal Gas Law I**

A sample of hydrogen gas (H_2) has a volume of 8.56 L at a temperature of 0ºC and a pressure of 1.5 atm. Calculate the moles of H_2 molecules present in this gas sample.

0.57 mol

Exercise 7 **Ideal Gas Law II**

Suppose we have a sample of ammonia gas with a volume of 3.5 L at a pressure of 1.68 atm. The gas is compressed to a volume of 1.35 L at a constant temperature. Use the ideal gas law to calculate the final pressure.

4.4 atm

Exercise 8 **Ideal Gas Law III**

A sample of methane gas that has a volume of 3.8 L at 5ºC is heated to 86ºC at constant pressure. Calculate its new volume.

4.9 L

Exercise 9 **Ideal Gas Law IV**

A sample of diborane gas (B_2H_6), a substance that bursts into flame when exposed to air, has a pressure of 345 torr at a temperature of -15ºC and a volume of 3.48 L. If conditions are changed so that the temperature is 36ºC and the pressure is 468 torr, what will be the volume of the sample?

3.07 L

Exercise 10 **Ideal Gas Law V**

A sample containing 0.35 mol argon gas at a temperature of 13ºC and a pressure of 568 torr is heated to 56ºC and a pressure of 897 torr. Calculate the change in volume that occurs.

decreases by 3 L

GAS STOICHIOMETRY

Use $PV = nRT$ to solve for the volume of one mole of gas at STP:

Look familiar? This is the **molar volume** of a gas at STP. Work stoichiometry problems using your favorite method, dimensional analysis, mole map, the table way…just work FAST! Use the ideal gas law to convert quantities that are NOT at STP.

Exercise 11 Gas Stoichiometry I

A sample of nitrogen gas has a volume of 1.75 L at STP. How many moles of N_2 are present?

7.81×10^{-2} mol N_2

Exercise 12 Gas Stoichiometry II

Quicklime (CaO) is produced by the thermal decomposition of calcium carbonate ($CaCO_3$). Calculate the volume of CO_2 at STP produced from the decomposition of 152 g $CaCO_3$ by the reaction

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

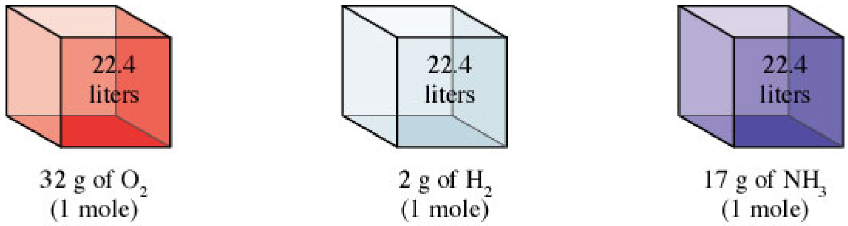
34.1 L CO_2 at STP

Exercise 13 Gas Stoichiometry III

A sample of methane gas having a volume of 2.80 L at 25ºC and 1.65 atm was mixed with a sample of oxygen gas having a volume of 35.0 L at 31ºC and 1.25 atm. The mixture was then ignited to form carbon dioxide and water. Calculate the volume of CO_2 formed at a pressure of 2.50 atm and a temperature of 125ºC.

2.47 L

THE DENSITY OF GASES:



$$d = \frac{m}{V} = \frac{P(MM)}{RT} \text{ \{for ONE mole of gas\}} = \frac{MM}{22.4\ L} \quad \text{AND} \quad \text{Molar Mass} = MM = \frac{dRT}{P}$$

"Molecular Mass kitty cat"—all good cats put dirt [*dRT*] over their pee [*P*]. Corny? Yep! But, you'll thank me later!

Just remember that densities of gases are reported in g/L NOT g/mL.

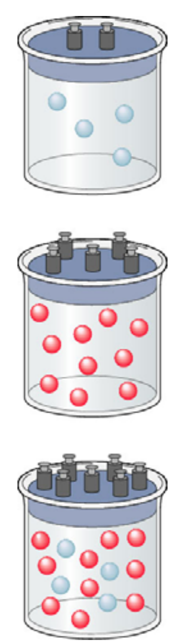
What is the approximate molar mass of air? _________

The density of air is approx. _______ g/L.
List 3 gases that float in air:
List 3 gases that sink in air:

Exercise 14 Gas Density/Molar Mass
The density of a gas was measured at 1.50 atm and 27ºC and found to be 1.95 g/L. Calculate the molar mass of the gas.

32.0 g/mol

GAS MIXTURES AND PARTIAL PRESSURES



The pressure of a mixture of gases is the sum of the pressures of the different components of the mixture:

$$P_{total} = P_1 + P_2 + \ldots P_n$$

John Dalton's Law of Partial Pressures also uses the concept of mole fraction, χ

$$\chi_A = \frac{\text{moles of A}}{\text{moles A + moles B + moles C + } \ldots}$$

so now, $P_A = \chi_A P_{total}$

The partial pressure of each gas in a mixture of gases in a container depends on the number of moles of that gas. The total pressure is the SUM of the partial pressures and depends on the total moles of gas particles present, no matter what they are!

Exercise 15 **Dalton's Law I**

Mixtures of helium and oxygen are used in scuba diving tanks to help prevent "the bends." For a particular dive, 46 L He at 25ºC and 1.0 atm and 12 L O_2 at 25ºC and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25ºC.

P_{He} = 9.3 atm
P_{O2} = 2.4 atm
P_{TOTAL} = 11.7 atm

Exercise 16 **Dalton's Law II**

The partial pressure of oxygen was observed to be 156 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O_2 present.

0.210

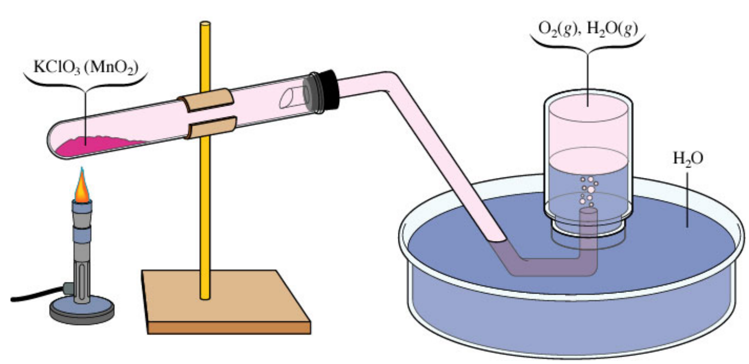
Exercise 17 **Dalton's Law III**

The mole fraction of nitrogen in the air is 0.7808. Calculate the partial pressure of N_2 in air when the atmospheric pressure is 760. torr.

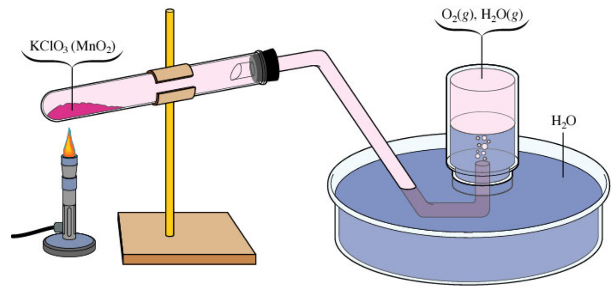
593 torr

WATER DISPLACEMENT

It is common to collect a gas by water displacement which means some of the pressure is due to water vapor collected as the gas was passing through! You must correct for this. You look up the partial pressure due to water vapor by knowing the ***temperature***.



Exercise 8 **Gas Collection over Water**



A sample of solid potassium chlorate ($KClO_3$) was heated in a test tube (see the figure above) and decomposed by the following reaction:

$$2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$$

The oxygen produced was collected by displacement of water at 22ºC at a total pressure of 754 torr. The volume of the gas collected was 0.650 L, and the vapor pressure of water at 22ºC is 21 torr. Calculate the partial pressure of O_2 in the gas collected and the mass of $KClO_3$ in the sample that was decomposed.

Partial pressure of O_2 = 733 torr
2.12 g $KClO_3$

KINETIC MOLECULAR THEORY OF GASES

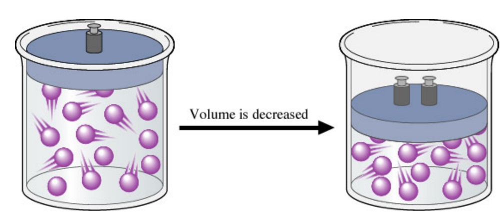
Assumptions of the MODEL:

1. All particles are in constant, random, motion.
2. All collisions between particles are perfectly elastic.
3. The volume of the particles in a gas is negligible
4. The average kinetic energy of the molecules is its Kelvin temperature.

This neglects any intermolecular forces as well.
Gases expand to fill their container, solids/liquids do not.
Gases are compressible, solids/liquids are not appreciably compressible.

This helps explain Boyle's Law:

If the volume is decreased that means that the gas particles will hit the wall more often, thus increasing pressure

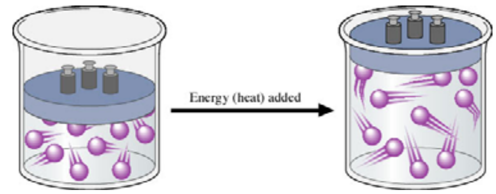


$$P = (nRT)\frac{1}{V}$$

Constant

And helps explain Charles' Law

When a gas is heated, the speed of its particles increase and thus hit the walls more often and with more force. The only way to keep the *P* constant is to increase the volume of the container.

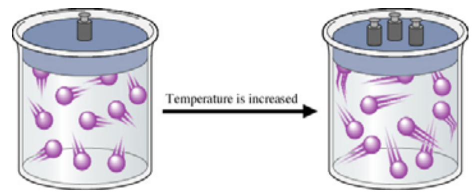


$$V = \left(\frac{nR}{P}\right)T$$

↑ Constant

And also helps explain Gay-Lussac's Law

When the temperature of a gas increases, the speeds of its particles increase, the particles are hitting the wall with greater force and greater frequency. Since the volume remains the same this would result in increased gas pressure.

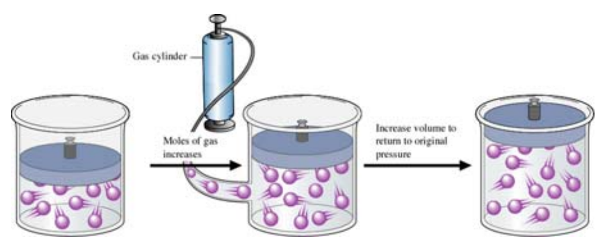


$$P = \left(\frac{nR}{V}\right)T$$

↑ Constant

And even helps explain Avogadro's Law

An increase in the number of particles at the same temperature would cause the pressure to increase if the volume were held constant. The only way to keep constant *P* is to vary the *V*.



$$V = \left(\frac{RT}{P}\right)n$$

↑ Constant

What about Dalton's Law? The *P* exerted by a *mixture* of gases is the SUM of the partial pressures since gas particles are acting *independent* of each other and the volumes of the individual particles DO NOT matter.

DISTRIBUTION OF MOLECULAR SPEEDS
Plot # of gas molecules having various speeds vs. the speed and you get a curve. Changing the temperature affects the *shape* of the curve NOT the area beneath it. Change the # of molecules and all bets are off!

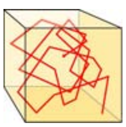
Maxwell's equation:

$$\sqrt{\overline{u^2}} = u_{rms} = \sqrt{\frac{3RT}{FW}}$$

Use the "energy R" or 8.314510 J/K• mol for this equation since kinetic energy is involved.

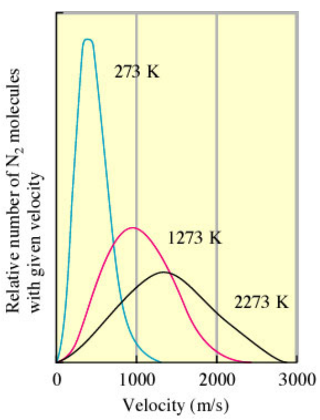
Exercise 19 **Root Mean Square Velocity**
Calculate the root mean square velocity for the atoms in a sample of helium gas at 25ºC.

1.36×10^3 m/s



If we could monitor the path of a single molecule it would be very erratic.

<u>Mean free path</u>—the average distance a particle travels between collisions. It's on the order of a tenth of a micrometer. WAAAAY SMALL!



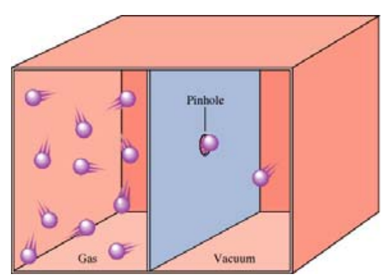
Examine the effect of temperature on the numbers of molecules with a given velocity as it relates to temperature.
HEAT 'EM UP, SPEED 'EM UP!!

Drop a vertical line from the peak of each of the three bell shaped curves—that point on the *x*-axis represents the AVERAGE velocity of the sample at that temperature. Note how the bells are "squashed" as the temperature increases. You may see graphs like this on the AP exam where you have to identify the highest temperature based on the shape of the graph!

GRAHAM'S LAW OF DIFFUSION AND EFFUSION

Effusion is closely related to diffusion. **<u>Diffusion</u>** is the term used to describe the mixing of gases. The ***rate*** of diffusion is the ***rate*** of the mixing.

<u>Effusion</u> is the term used to describe the passage of a gas through a tiny orifice into an evacuated chamber as shown on the right.
The rate of effusion measures the speed at which the gas is transferred into the chamber.



The rates of effusion of two gases are inversely proportional to the square roots of their molar masses at the same temperature and pressure.

$$\frac{\text{Rate of effusion of gas 1}}{\text{Rate of effusion of gas 2}} = \sqrt{\frac{MM_2}{MM_1}}$$

REMEMBER ***rate*** is a change in a quantity over time, NOT just the time!

Exercise 20 Effusion Rates

Calculate the ratio of the effusion rates of hydrogen gas (H_2) and uranium hexafluoride (UF_6), a gas used in the enrichment process to produce fuel for nuclear reactors.

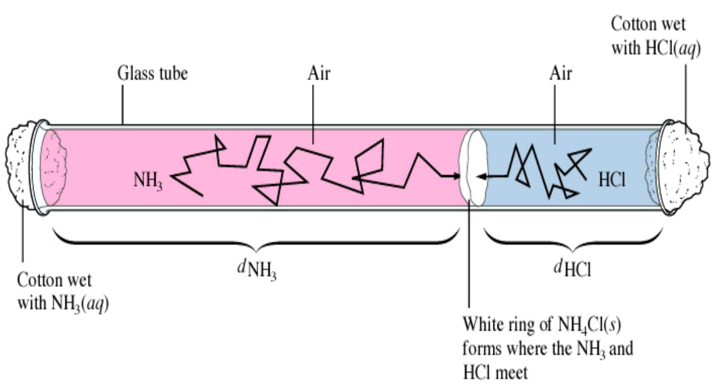
13.2

Exercise

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

Diffusion

This is a classic!



$$\frac{\text{Distance traveled by } NH_3}{\text{Distance traveled by HCl}} = \frac{u_{rms} \text{ for } NH_3}{u_{rms} \text{ for HCl}} = \sqrt{\frac{MM_{HCl}}{MM_{NH_3}}} = \sqrt{\frac{36.5}{17}} = 1.5$$

The observed ratio is LESS than a 1.5 distance ratio—why?

This diffusion is slow considering the molecular velocities are 450 and 660 meters per second—which one is which?

This tube contains air and all those collisions slow the process down in the real world. Speaking of real world….

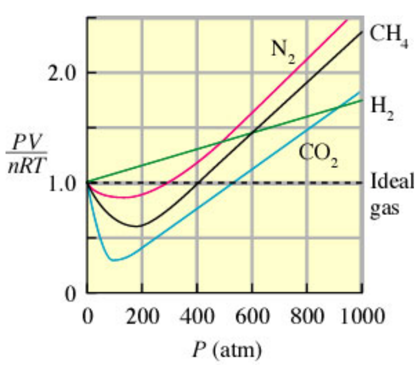
REAL, thus *NON*IDEAL GASES
Most gases behave ideally until you reach high pressure and low temperature. (By the way, either of these can cause a gas to liquefy, go figure!)

van der Waals Equation--corrects for negligible volume of molecules and accounts for inelastic collisions leading to intermolecular forces (his real claim to fame).

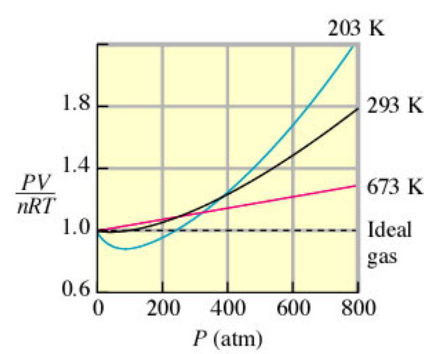
$$[P + a(\frac{n}{V})^2][V - bn] = nRT$$

a and *b* are van der Waals constants; no need to work problems, it's the concepts that are important! Notice pressure is increased (intermolecular forces lower real pressure, you're correcting for this) and volume is decreased (corrects the container to a smaller "free" volume).

These graphs are classics and make great multiple choice questions on the AP exam.



When PV/nRT = 1.0, the gas is ideal
All of these are at 200K.
Note the P's where the curves cross the dashed line [ideality].



This graph is just for nitrogen gas.
Note that although nonideal behavior is evident at each temperature, the deviations are smaller at the higher Ts.

Don't underestimate the power of understanding these graphs. We love to ask question comparing the behavior of ideal and real gases. It's not likely you'll be asked an entire free-response gas problem on the real exam in May. Gas Laws are tested extensively in the multiple choice since it's easy to write questions involving them! You will most likely see $PV = nRT$ as one part of a problem in the free-response, just not a whole problem!

GO FORTH AND RACK UP THOSE MULTIPLE CHOICE POINTS!!