

AP* Chemistry GASES

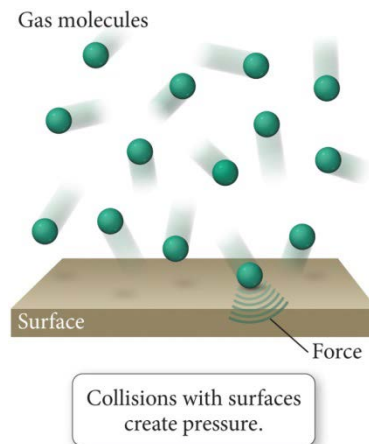
The gaseous state of matter is the simplest and best-understood state of matter. You inhale approximately 8,500 L of air each day. This amounts to about 25 lbs of air. Breathing is a three-step process: inhaling, gas exchange with the circulatory system, and exhaling. Approximately 80% pressure differences created by your body allow you to breathe. Nearly the Earth's entire atmosphere is made up of only five gases: nitrogen, oxygen, water vapor, argon, and carbon dioxide.

PROPERTIES OF GASES

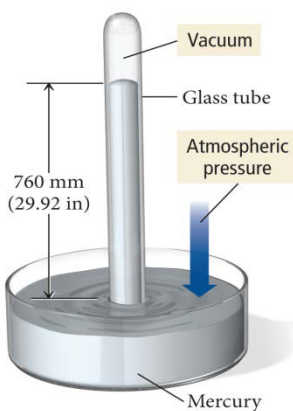
Only **FOUR** quantities are needed to define the **state of a gas**:

1. the quantity of the gas, n (in moles)
2. the *temperature* of the gas, T (**in KELVINS**)
3. the *volume* of the gas, V (in liters)
4. the *pressure* of the gas, P (in atmospheres)

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



The Mercury Barometer



Pressure and Density



GAS PRESSURE is 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 \times acceleration; (Newton's 2nd Law)

The SI units follow:

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

Pressure-- Force/ unit area; N/m^2 ; which is the definition of 1.0 Pascal

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

1 mm of Hg = 1 torr

$$1.00 \text{ atm} = 760.00 \text{ mm Hg} = 760.00 \text{ torr} = 29.92 \text{ in Hg} = 14.7 \text{ psi} = 101.325 \text{ kPa} \approx 10^5 \text{ Pa}$$

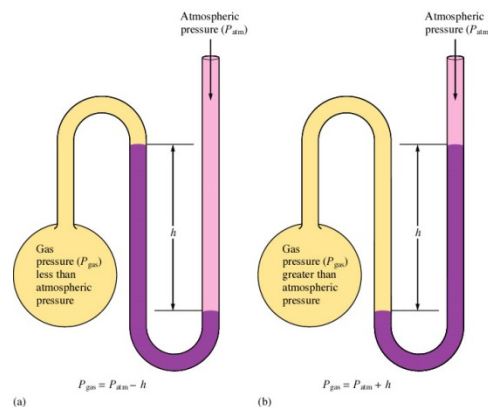
At sea level all of the above define STANDARD PRESSURE.

The SI unit of pressure is the Pascal (named after Blaise Pascal);

$$1 \text{ Pa} = 1 \text{ N} / \text{m}^2$$

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.

Exercise 2 Pressure Comparisons

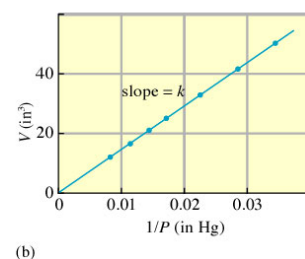
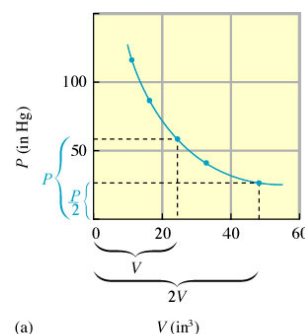
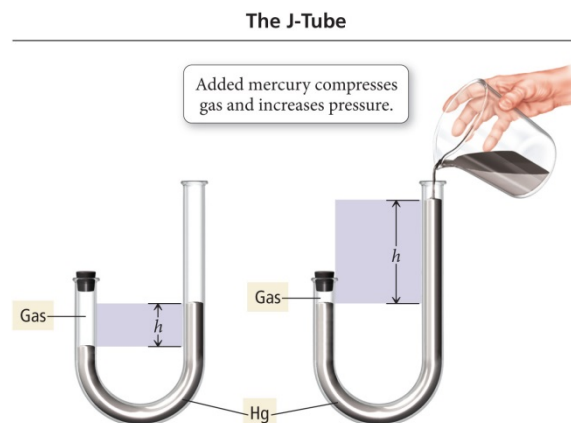
Rank the following pressures in decreasing order of magnitude (largest first, smallest last): 75 kPa, 300. torr, 0.60 atm and 350. mm Hg.

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.*

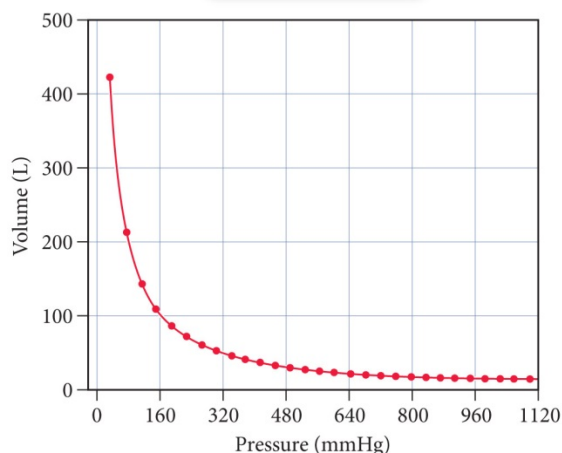
ALL GASES BEHAVE IN THIS MANNER!

- Robert Boyle was an Irish chemist. He studied PV relationships using a J-tube set up in the multi-story entryway of his home. (Thus his was MUCH larger than the one shown right.)
 - $P \propto 1/V$
 - \therefore pressure and volume are **inversely** proportional
 - Volume \uparrow Pressure \downarrow **at constant temperature**, the converse is also true
 - *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 $m = \text{slope}$, and b is 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 originally collected is graphed on (a) above on the right.
- $P_1V_1 = P_2V_2$ is the easiest form of Boyle's law to **memorize**
- Boyle's Law has been tested for over three centuries. It holds true **only at low pressures**.

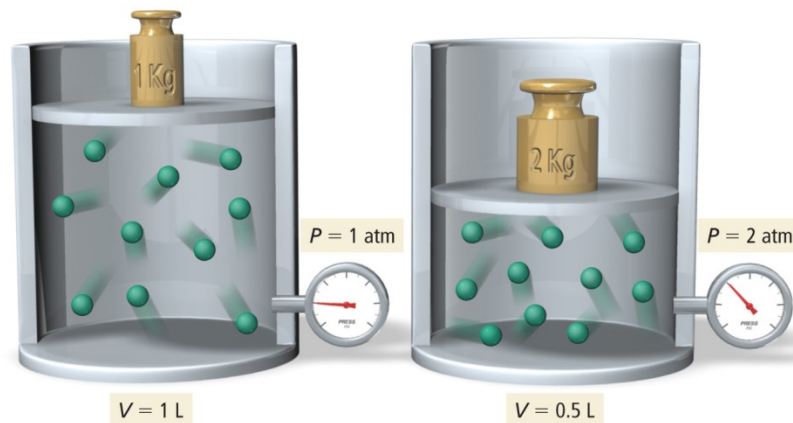


Boyle's Law

As pressure increases, volume decreases.



Volume versus Pressure: A Molecular View



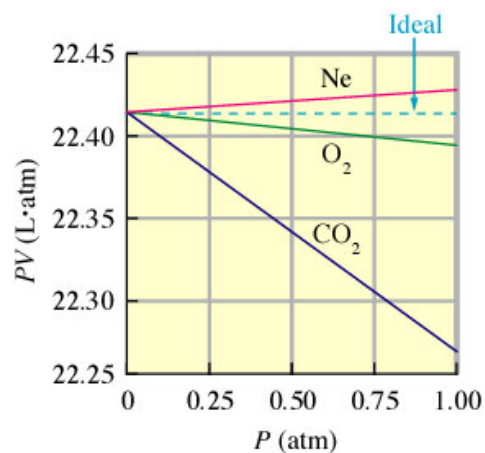
Exercise 3 Boyle's Law I

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?

Ideal Gases

At “normal” conditions such as standard temperature and pressure, most real gases behave qualitatively like an ideal gas. Many gases such as nitrogen, oxygen, hydrogen, noble gases, and some heavier gases like carbon dioxide can be treated like ideal gases within reasonable tolerances. Generally, a gas behaves more like an ideal gas at higher temperature and lower pressure, as the work which is against intermolecular forces becomes less significant compared with the particles' kinetic energy, and the size of the molecules becomes less significant compared to the empty space between them.

An **ideal** gas is expected to have a constant value of PV , as shown by the dotted line on the graph pictured right. 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. So, why does CO_2 deviate from ideal behavior the most? It has more electrons, thus is more polarizable, thus has higher dispersion forces (a type of intermolecular force a.k.a. London dispersion forces or LDFs), therefore the molecules are more attracted to each other, so carbon dioxide gas deviates from ideal behavior more than oxygen or carbon dioxide does.



Exercise 4 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 0°C . Using the results listed below; calculate the Boyle's law constant for NH_3 at the various pressures. Calculate the deviation from ideal behavior in each case. Account for the trend apparent in the data.

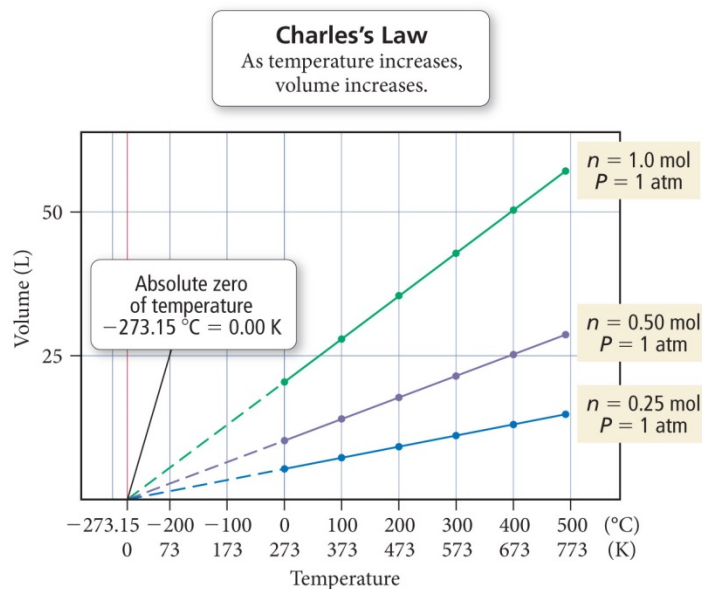
<i>Experiment</i>	<i>Pressure (atm)</i>	<i>Volume (L)</i>
1	0.1300	172.1
2	0.2500	89.28
3	0.3000	74.35
4	0.5000	44.49
5	0.7500	29.55
6	1.000	22.08

Exercise 5 Boyle's Law III

Next, PLOT the values of PV vs. P for the six experiments in **Exercise 4**. Extrapolate to determine what PV equals at a *hypothetical* 0.00 atm pressure. Compare it to the PV vs. P graph on page 3 of these lecture notes. What is the value of the y-intercept?

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 KELVINS Why?*

- Jacques Charles was a French physicist and the first person to fill a hot “air” balloon with hydrogen gas and made the first solo hot air balloon flight!
 - $V \propto T$ plot = straight line
 - $V_1T_2 = V_2T_1$
 - Temperature \propto Volume **at constant pressure**
 - 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.
 - What is the *temperature* when the *volume* extrapolates to zero? Sound familiar?

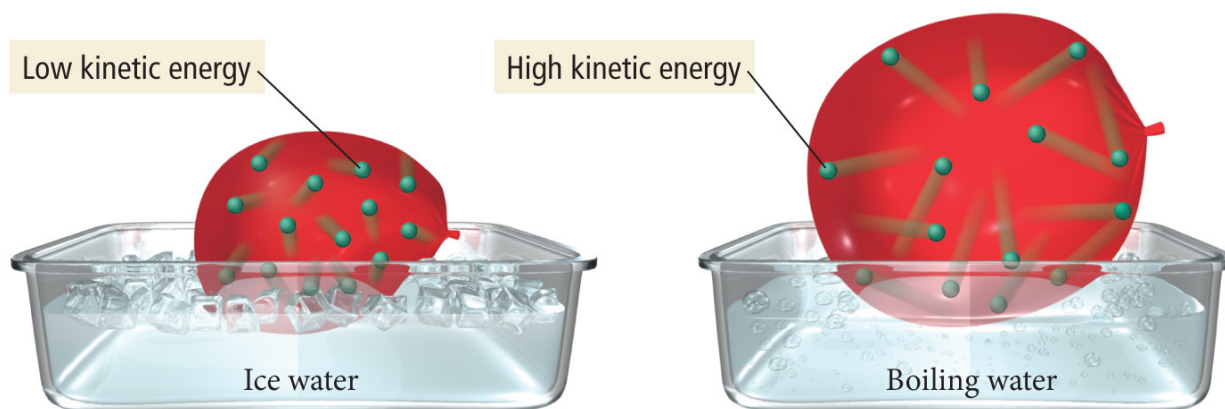


Exercise 6 Charles's Law

A sample of gas at 15°C and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38°C and 1 atm?

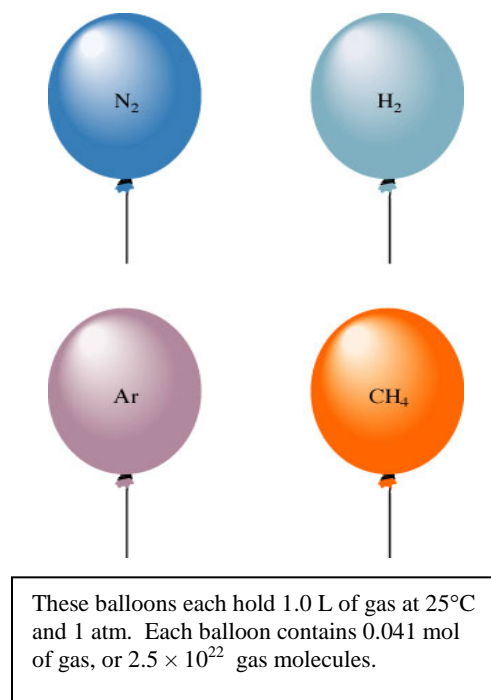
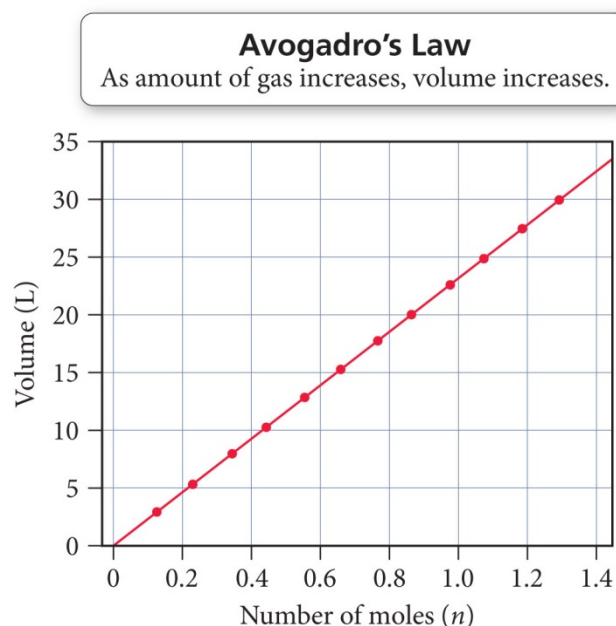
Each of the balloons below contains the same number of particles in the gas phase. This is yet another example of “heat ‘em up and speed ‘em up!”. As the molecules warm, they gain kinetic energy, move faster, and thus collide with the walls of their container with more energy. (Umph! If you prefer) In this case, the “walls” of the container are made of rubber which can expand and contract.

Volume versus Temperature: A Molecular View



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.*

- $V \propto n$
- $n \propto \text{Volume}$ **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 just this use a simple pattern to figure the rest out:

- Place the scientist names in alphabetical order.
- Boyle's Law uses the first 2 variables, Charles' Law the second 2 variables & Gay-Lussac's Law the remaining combination of variables.
Whichever variable doesn't appear in the formula is being held CONSTANT!

Exercise 7 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 25°C. 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?

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 *is an equation of state*.

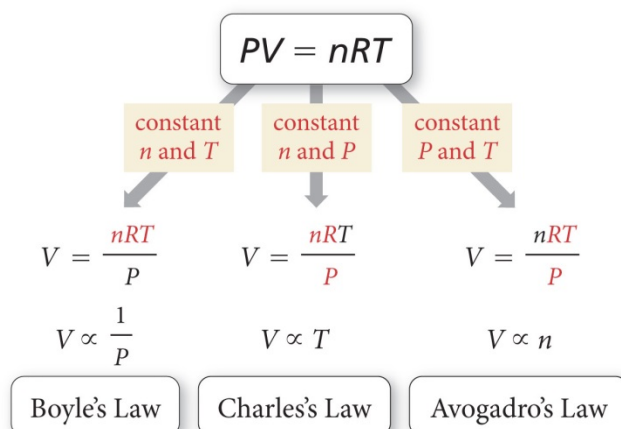
$R = 0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$ also expressed as $0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$

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!

Ideal Gas Law



Exercise 8 Ideal Gas Law I

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

Exercise 9 Which Gas Law?

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.

Exercise 10 Which Gas Law?

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

Exercise 11 **Which Gas Law?**

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 $-15^\circ C$ and a volume of 3.48 L. If conditions are changed so that the temperature is $36^\circ C$ and the pressure is 468 torr, what will be the volume of the sample?

Exercise 12 **Ideal Gas Law II**

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

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 13 **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?

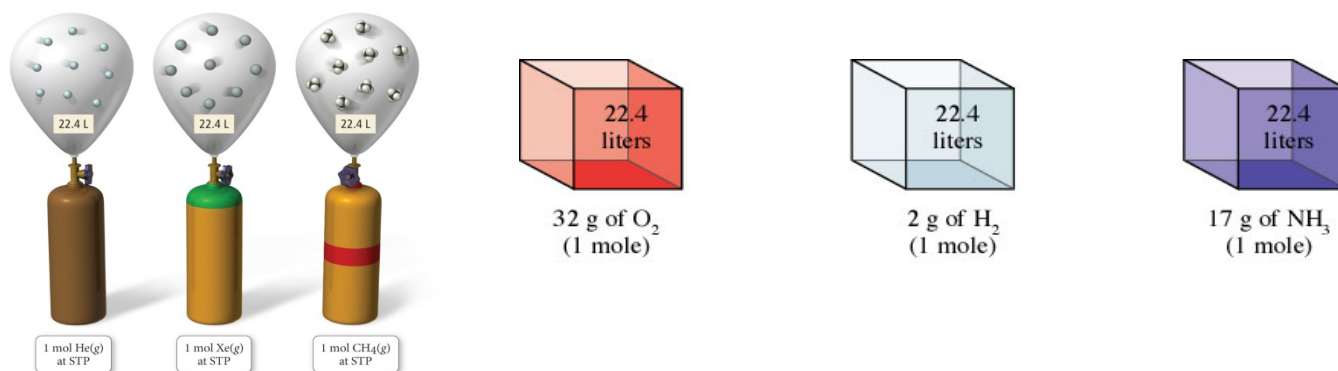
Exercise 14 Gas Stoichiometry II

Quicklime (CaO) is produced by the thermal decomposition of calcium carbonate (CaCO₃). Calculate the volume of CO₂ at STP produced from the decomposition of 152 g CaCO₃ by the reaction

**Exercise 15 Gas Stoichiometry III**

A sample of methane gas having a volume of 2.80 L at 25°C and 1.65 atm was mixed with a sample of oxygen gas having a volume of 35.0 L at 31°C and 1.25 atm. The mixture was then ignited to form carbon dioxide and water. Calculate the volume of CO₂ formed at a pressure of 2.50 atm and a temperature of 125°C.

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! Crude and socially unacceptable? You bet! But ... you’ll thank me later when you’re flying through such gas law problems.

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

What is the approximate molar mass of air expressed in g/L?

List 3 gases that float in air:

List 3 gases that sink in air:

Exercise 16 Gas Density/Molar Mass

The density of a gas was measured at 1.50 atm and 27°C and found to be 1.95 g/L. Calculate the molar mass of the gas.

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:

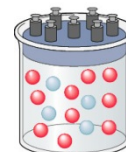
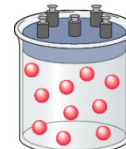
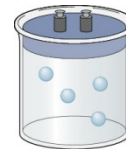
$$P_{total} = P_1 + P_2 + \dots + P_n$$

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

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

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 17 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 25°C and 1.0 atm and 12 L O₂ at 25°C 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 25°C.

Exercise 18 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 O₂ present.

Exercise 19 Dalton's Law III

The mole fraction of nitrogen in the air is 0.7808. Calculate the partial pressure of N₂ in air when the atmospheric pressure is 760. torr.

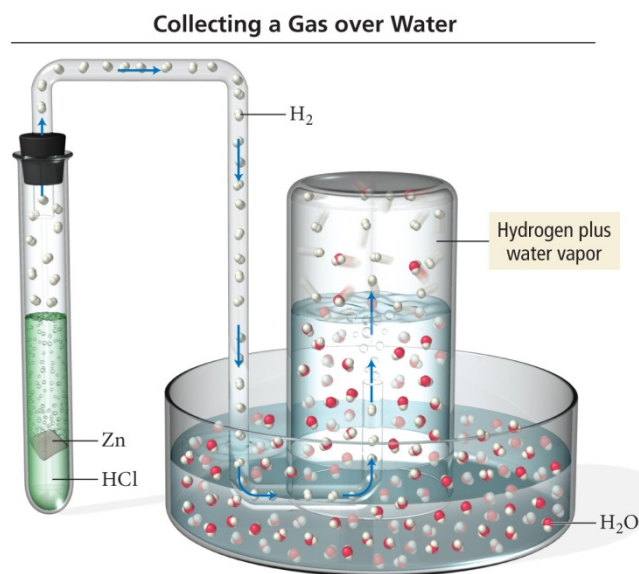
WATER DISPLACEMENT

It is common to collect a gas in the laboratory by water displacement. The confounding factor is that some of the pressure in the collection vessel is due to water vapor collected as the gas was passing through!

You must correct for this in order to report the P of "dry" gas.

How? You simply look up the partial pressure due to water vapor at a given temperature and subtract that value from the total pressure.

The experiment pictured is a classic! You may have done it with Mg rather than zinc and used a eudiometer or inverted and sealed buret to measure the volume of the gas collected "over water".



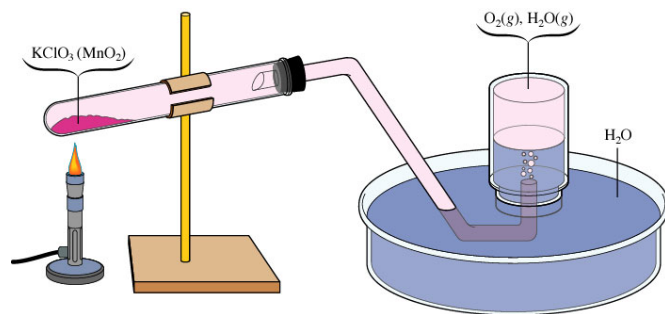
Exercise 20

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:



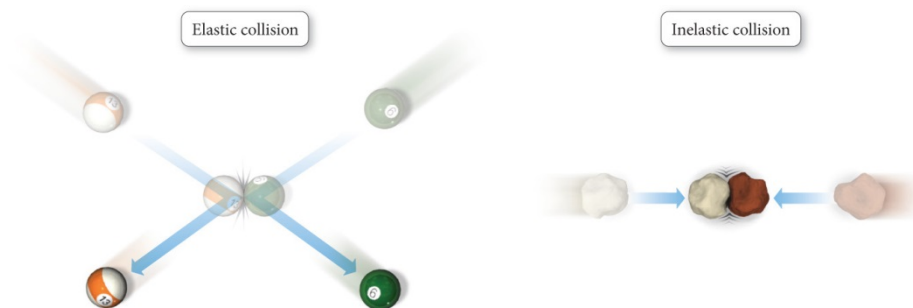
The oxygen produced was collected by displacement of water at 22°C at a total pressure of 754 torr. The volume of the gas collected was 0.650 L, and the vapor pressure of water at 22°C is 21 torr. Calculate the partial pressure of O_2 in the gas collected and the mass of KClO_3 in the sample that was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



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.



Kinetic Molecular Theory



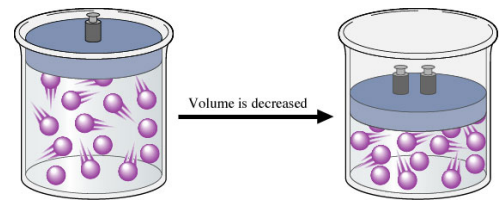
This theory neglects any intermolecular forces as well. And it is important to note that gases expand to fill their container, solids/liquids do not. And that gases are compressible; solids/liquids are not appreciably compressible.

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

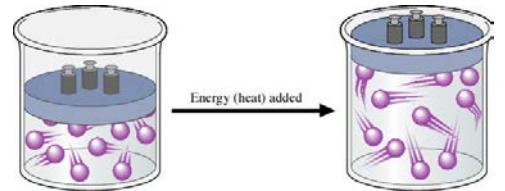


And also helps explain Charles' Law

When a gas is heated, the speeds 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

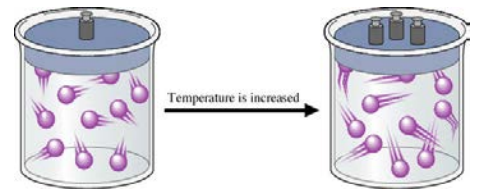


Yep, you guessed it! It also helps explain Gay-Lussac's Law

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

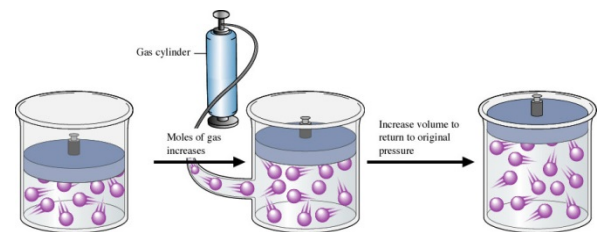


And it even helps explain Avogadro's Law

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:

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

Use the “energy R ” or $8.314510 \text{ J/K}\bullet \text{ mol}$ for this equation since kinetic energy is involved.

Exercise 21 Root Mean Square Velocity

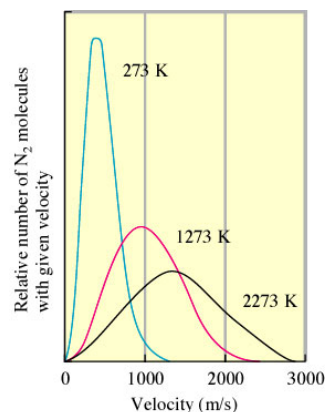
Calculate the root mean square velocity for the atoms in a sample of helium gas at 25°C .

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

Mean free path—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.

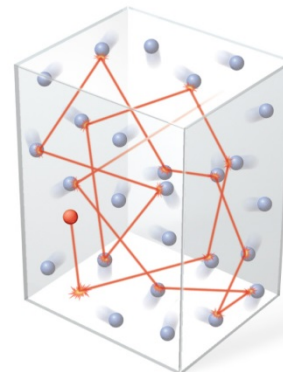
HEAT 'EM UP, SPEED 'EM UP!!



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!

Typical Gas Molecule Path

The average distance between collisions is the mean free path.

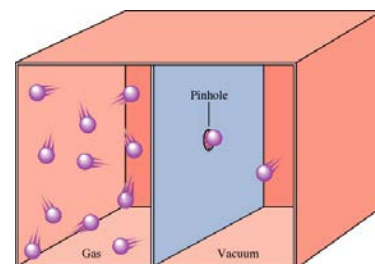


GRAHAM'S LAW OF DIFFUSION AND EFFUSION

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

Effusion 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 22 Effusion Rates

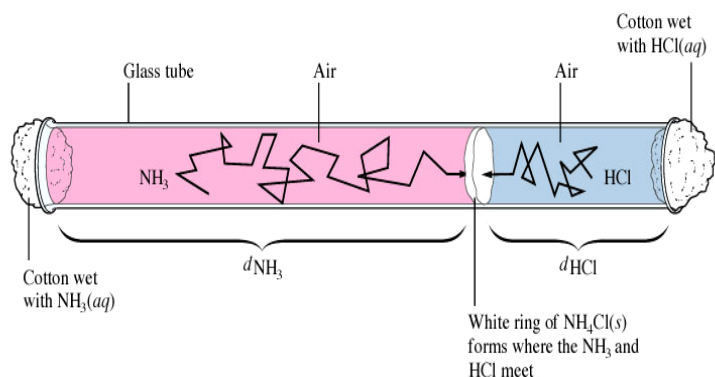
Calculate the ratio of the effusion rates of hydrogen gas (H₂) and uranium hexafluoride (UF₆), a gas used in the enrichment process to produce fuel for nuclear reactors.

Exercise 23

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! <https://www.youtube.com/watch?v=GRcZNCa9DxE> (animation) Effusion of a Gas:
<http://www.youtube.com/watch?v=0uBK7VxT00E>
<https://www.youtube.com/watch?v=o7C4lo5n0zU> (actual, but not great)



$$\frac{\text{Distance traveled by NH}_3}{\text{Distance traveled by HCl}} = \frac{u_{\text{rms for NH}_3}}{u_{\text{rms for HCl}}} = \sqrt{\frac{MM_{\text{HCl}}}{MM_{\text{NH}_3}}} = \sqrt{\frac{36.5}{17}} = 1.5$$

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

This diffusion is slow despite 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 NONIDEAL GASES

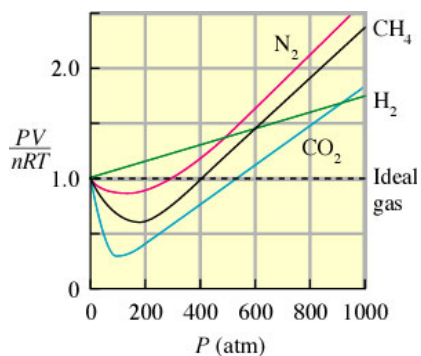
Most gases behave ideally until you reach high pressure and low temperature. (By the way, either of these can cause a gas to liquefy, go figure!)

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

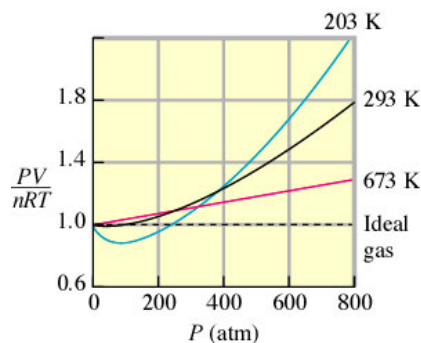
$$\left[P + a \left(\frac{n}{V} \right)^2 \right] [V - bn] = nRT$$

The coefficients 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!!

And, just for fun:

Collapsing Can: <http://www.graspr.com/videos/The-Collapsing-Can-1>

Shall we try a bigger can? <http://www.youtube.com/watch?v=Uy-SN5j1ogk&NR=1>

How about the biggest can we can find? http://www.youtube.com/watch?v=E_hci9vrvfw

Boiling water with ice: <http://www.youtube.com/watch?v=zzVtbvVS2IQ>

Cooling gases with liquid nitrogen MIT: <http://www.youtube.com/watch?v=ZvrJgGhnmJo>

Getting a boiled egg into a bottle: <http://www.youtube.com/watch?v=xZdfcRiDs8I&NR=1&feature=fvwp>

Gravity has nothing to do with it! <http://www.youtube.com/watch?v=BofIBaYk5e0&feature=related>

Getting egg OUT of bottle! <http://www.youtube.com/watch?v=x--4l-SL77Y&feature=related>

Peeps in a vacuum: <http://www.youtube.com/watch?v=lfNJEdKgLU&NR=1>

and another: <http://www.youtube.com/watch?v=ciPr4Tg9k78&feature=related>

Ideal Gas Law: <http://www.youtube.com/watch?v=Myvtv0wlZK8&feature=related>

Diffusion of ammonia and HCl (animation): <http://www.youtube.com/watch?v=L41KhBPBmYA&feature=related>

Diffusion of ammonia and HCl (real deal): <http://www.youtube.com/watch?v=WAJAslkwolk&feature=related>

Putting it all together:

http://www.mhhe.com/physsci/chemistry/animations/chang_7e_esp/gam2s2_6.swf

Why R as in $PV = nRT$?

This is the kind of stuff that drives me crazy as well! I went in search of the answer some time ago, so I'll share what I found:

As usual, the answer relates to a history lesson. It was Clausius in the mid 1800's that refined the conversion factor for converting degrees Celsius to Kelvins (from adding 267 to adding 273 to the Celsius temperature. He did so using the careful experimental data of another French scientist, Regnault.

Clausius also noted that Regnault's data indicated that the farther the temperature and pressure conditions were from the condensation point of the gas, the more correctly the Ideal Gas Law applies. So, there is speculation that the "constant" was assigned the letter "R" to honor Regnault's work.

In the spirit of giving credit where credit is due, my source was a Journal of Chem. Ed article written by William B. Jensen Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172