Chapter 10 – Gases

We have talked a little about gases in Chapter 3 and we dealt briefly with them in our stoichiometric calculations in Chapter 7. In this chapter we will explore more about gases as even see where we came up with that 1 mole = 22.4 L at STP relationship that I included with my "bubble chart".

Section 10-1: The Nature of Gases and the Kinetic Molecular Theory

1) Sec 10-1.1 – The Properties of Gases

Basic assumptions of the properties of gases:

a) Gases always spread out to fill the shape and volume of whatever space is available, so the volume of a gas is always the same as the volume of its container.

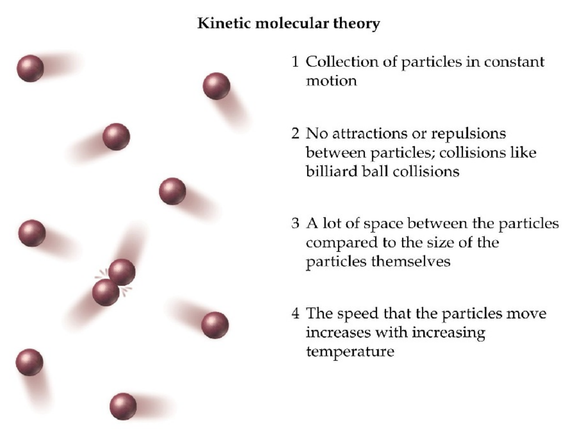
b) Gases mix rapidly and thoroughly as the particles move in their container.

c) Gases are compressible so that we can keep putting the same amount of a gas into smaller and smaller containers.

d) Gases have low densities as compared to solids or liquids.

2) Sec 10-1.2 – The Kinetic Molecular Theory

The gaseous state of matter is quite different from the other two physical states. Gases are composed of either individual atoms (in the case of noble gases) or molecules (for all gaseous diatomic elements and other gaseous compounds). This fact and others can be summarized in a set of assumptions collectively known as the **kinetic molecular theory**, or simply the **kinetic theory**. The kinetic theory was advanced in the late nineteenth century to explain the common properties of gases. It allows us to visualize the behavior of gases at the molecular level.



The kinetic theory can be summarized:

a) Gases are composed of tiny particles (atoms or molecules) whose volume is negligible compared to the volume of the container they occupy. This means that the volume of a gas is mostly empty space.

b) The particles in a gas move rapidly (average speed of air particles at room temperature is about 1000 meters/sec) in constant random motion.

c) The collisions that take place between gas particles with others or the walls of the container are said to be "completely elastic" (nothing is lost or gained).

d) Gas particles have virtually no attractive or repulsive forces between them.

e) The average kinetic energy of the particles of a gaseous substance is proportional to the absolute or Kelvin temperature of the substance (K = °C +273). Also, at the same temperature, different gases have the same average kinetic energy.

3) Sec 10-1.3 – Graham' Law

The equation for the kinetic energy of a gas – $K.E. = ½\, mv^2$ – implies that, since gases have the same kinetic energies at the same temperature, the relative velocities relate to their molar masses.

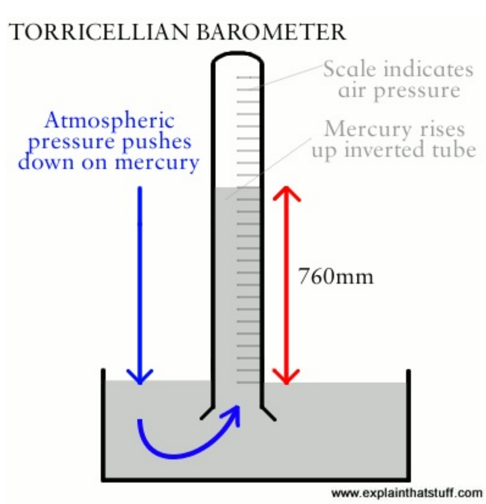
The average velocities of gases relate to two other aspects of molecular motion - the rate of ***diffusion*** *(mixing)* and the rate of ***effusion*** *(moving through an opening or hole)*. The rate of diffusion is described by **Graham's Law** which states that *the rates of diffusion of different gases at the same temperature are inversely proportional to the square roots of their molar masses*.

We have experienced this: Think of two balloons - one filled with helium and one filled with air. The helium balloon will decrease in size faster than a similar balloon filled with air.

Section 10-2: The Pressure of a Gas

4) Sec 10-2.1 – The Barometer and Pressure

The barometer was invented by Evangelista Torricelli in 1643 using a tube filled with mercury inverted into a pool of mercury. Aside from the instruments people use these days, the best tool is still this classic barometer.



Some terms:

a) Pressure is a result of the collisions of the gas particles with the sides of its container and is the force exerted per unit area (e.g.., lbs/in^2).

b) Vacuum – The resulting empty space when no gas particles are present.

c) Existence of Air Pressure -- soda cans, balloon in a bottle, can.

d) Measurement of Atmospheric Pressure – The barometer measures air pressure by determining the height of a column of mercury (d=13.6 g/cc) which can be supported by the air pressure.

e) Units of pressure (mm Hg, in Hg, atmospheres, lbs/in^2, kilopascals, torr)

   1 atm = 760 mm Hg = 760 torr = 29.9 in Hg = 14.7 lbs/in^2 = 101.3 kPa

f) When you work with gases, standard conditions (STP) are defined as a temperature of 0°C and a pressure of 760 mm Hg, 1 atm or 101.3 kPa.

g) 1 atmosphere of pressure is the average pressure measured at sea level and is the standard for pressure.

Examples

1) Convert 190 mm Hg to atmospheres

2) Convert 190 mm Hg to KPa
   Either: Or:

3) Convert 720 mm Hg to lbs/in^2

5) The Effect of Adding or Removing a Gas

a) If the number of gas molecules is doubled and the temperature and volume of the gas remain constant, the pressure will also double. That is, the pressure exerted by the gas is directly proportional to the amount of gas in the container. This is logical if one remembers that pressure is the result of the collisions between the gas particles and the walls of the container (think: lb/in^2 – force per unit area). If one doubles the number of collisions, the pressure should also double.

b) If the number of gas molecules is doubled and the volume is free to change, the pressure of the gas will be the same as the outside pressure. The volume will double, assuming that the temperature and pressure of the gas did not change.

6) Sec 10-2.2 – Boyle's Law - 1662 (Robert Boyle, 1627-1691)

Reducing the volume of the container causes an increase in the gas pressure, and increasing the volume of the container causes a decrease in the gas pressure.

Boyle's Law – At constant temperature, the volume of a given mass of gas varies inversely with the pressure. $P \times V = \text{constant}$ or in a more useful form $P_1V_1 = P_2V_2$

Or, stated another way, *there is an inverse relationship between the pressure exerted by a sample of gas and its volume if the temperature is held constant*.

We can use this relationship to see what happens to a given sample of gas if either the volume or pressure are changed (as long as the temperature is constant). What happens when you use a tire pump?

Example: If a gas has a volume of 10 liters at a pressure of 2.0 atm, what must the volume change to in order for the pressure to be 6.5 atm?

Secton 10-3: Charles', Gay-Lussac's, and Avogadro's Laws

Raising the temperature of a gas in a container either causes an increase in the pressure (if the volume of the container is fixed – cannot expand) or causes an increase in the volume of the container (if the container is free to expand). Since the average kinetic energy increases in proportion to the increase in the Kelvin temperature, the increase in either the pressure or the volume is directly proportional to the increase in the Kelvin temperature.

[Remember that the Kelvin temperature has no negative values. (There are also no negative values for pressure and volume if you think about it.)]

7) Sec 10-3.1 – Charles' Law - 1780's (Jacques Charles 1746-1823)

Charles' Law – At constant pressure, the volume of a given mass of gas varies directly with the absolute or Kelvin temperature. $V \propto T$

$$\frac{V}{T} = \text{constant} \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

This expression can be used to calculate how the volume of a given sample of gas changes as the temperature changes if the pressure is held constant.

Example: If a balloon has a volume of 10 Liters at 22°C, to what volume will it expand to at 86°C?

8) Sec 10-3.2 – Gay-Lussac's Law - 1802 (Joseph Gay-Lussac, 1778-1850)

What happens if we hold the volume of a gas constant and vary the pressure an temperature? In the extreme, there will be an explosion if the container cannot hold the pressure and it breaks.

Gay-Lussac's Law – At constant volume, the pressure exerted by a given mass of gas varies directly with the absolute or Kelvin temperature. $P \propto T$

$$\frac{P}{T} = \text{constant} \qquad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Note: I sometimes refer to this as Gay-Lussac's First Law because there is another law that is also attributed to him that we will discuss later in this chapter.

Example: If the pressure of acetylene in a steel cylinder is 200 lbs/in^2 at a temperature of 0°C, what will be the pressure at 37°C?

9) Sec 10-3.3 – The Combined Gas Law

What happens if we have a sample of a gas and we want to change both the pressure and temperature? We could do the calculation for Boyle's Law and then take that result and apply Charles' Law. Likewise we could do a similar set of calculations if we wanted to see what happened if we changed the volume and temperature. These approaches are not the most convenient but they would work.

OR: The three gas laws just discussed can be combined into a single expression called the **Combined Gas Law**. This is not really a new law but a logical combination of the others.

Combined Gas Law – For a given mass of gas, the product of its pressure and volume divided by its Kelvin temperature is a constant.

$$\frac{P \times V}{T} = \text{constant} \qquad \frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$$

We can now work problems more easily when we have simultaneous changes in any two of the three conditions.

Note one important watchout: Aside from the fact that temperature ALWAYS is used in terms of the Kelvin scale, we must also remember that the units for pressure and volume MUST BE THE SAME on both sides of the equation. (It does not matter what units are used, just that they are the same – other than what is asked for in the problem.)

This relationship is often used when different scientists want to compare identical reactions run under different conditions of temperature and pressure. Think about what would happen if we ran a gas reaction in Saint Louis, the identical reaction was run in

Denver (St. Mary's), and also in Houston (Loretto Academy). When the results were in we likely would want to compare them but, chances are, even if we had the exact same amount of gas our results would be different because of the differences in pressure and temperature in the three locations. We could all recalculate all the results to match the other conditions, but it might be simpler for each to express the results of experiments in terms of uniform STP (Standard Temperature and Pressure) conditions.

This latter is the most common way we express the results of a gas experiment.

Example: Calculate the volume of a gas at 0°C and 760 mm Hg, if the volume of the gas was 500 mL when the gas was collected at 22°C and 720 mm Hg.

10) Sec 10-3.4 – Avogadro's Law - 1811 (Amedeo Avogadro 1776 - 1856)

This is sometimes referred to as Avogadro's Hypothesis or Principle as well as Law.

Volume and Moles – Equal volumes of gases at the same temperature and pressure contain equal numbers of particles. For example, at STP 22.4 L of any gas contains 1 mole or 6.02×10^{23} particles of gas. Note that this relates to the earlier mention of the relationship between volume and the amount of a gas.

The simple relationship is $\frac{V}{n} = \text{constant}$ and $\frac{V_1}{n_1} = \frac{V_2}{n_2}$

Example: What would be the new volume of a balloon if you added 2.1 moles of gas to a balloon that originally had 2.6 moles of gas and a volume of 28.0 liters if the pressure and temperature are constant?

11) Pressure and Moles – One could easily also realize that there is a similar relationship between pressure and moles if volume and temperature are constant, although we do not usually give this relationship or law a specific name.

Section 10-4: The Ideal Gas Law

12) Sec 10-4.1 – The Derivation of the Ideal Gas Law

What would we do if we wanted to increase the volume of a gas? We can see that we have several options – change the pressure (Boyle's Law), change the temperature (Charles' Law), and/or change the amount (moles) of gas (Avogadro's Law).

If we look at all the variables and extend the combined gas law we can think about a law that combines the four physical properties (pressure, volume, temperature, and moles) for gases into one equation.

If one combines the laws, the expression becomes $\frac{PV}{nT}$ = constant = **R**

Where R is the combined proportionality constant and is called the **universal gas constant** and unlike the previous constant values, this is a true constant that never varies.
If one then turns this around, we have what we call the **ideal gas law** in its usual form:

PV = nRT P = pressure V = volume in liters
n = moles of gas T = temperature in K

R is truly a constant. Its numeric value depends upon the units of pressure and volume that are used for the calculation. Thus,

R = 0.0821 L-atm/mole-K = 8.31 L-KPa/mole-K = 62.4 L-mm Hg/mole-K

and one can convert between the various R values by converting between the pressure units. Further, since $n = \frac{m}{MM}$ Then $\mathbf{PV = \frac{mRT}{MM}}$ m = mass in grams
MM = molar mass (g/mole)

If mass is given or needed, then use the second equation; if moles are given or needed, then use the first equation.

Examples:

a) You fill a rigid steel cylinder with a volume of 20 L of nitrogen gas to a pressure of 20,0000 KPa at 27°C. How many moles of nitrogen does the cylinder contain?

b) What is the volume of 1 mole of a gas at STP?

c) Calculate the mass in grams of CO_2, if 200 mL were collected at a temperature of 22°C and a total pressure of 755 mm Hg.

d) What pressure will be exerted by 25.5 g of ammonia, NH_3, gas at 25°C in a 5.0 L container?

13) The Weinkauff Modification of the Ideal Gas Law

When looking at the ideal gas law, one can also see how we could arrange it in proportions the way we did the other laws to make comparisons or changes. The resulting statement would be:

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

If one remembers the ideal gas law itself and then this statement, one can have all the other laws readily and answer most gas questions.

* We have already talked about the ways the ideal gas law itself can be used.

* If the number of moles and temperature are constant, the statement just becomes Boyle's Law.

* If the number of moles and the pressure are constant, then we have Charles' Law.

* If the pressure and temperature are constant, then we have Avogadro's Law.

14) Sec 10-4.2 – The Meaning of an Ideal Gas

The Ideal Gas Law is based on the assumptions of the kinetic molecular theory which does look at gases in an ideal situation. We do live in the real world, with real gases.

A gas that adheres to the gas laws at some conditions of temperature and pressure is said to exhibit ideal behavior. No gas behaves ideally, however, at all temperatures and pressures. The conditions at which gases behave ideally are at high temperatures (well above the boiling point of the substance) and at low pressure. Gases do not obey the gas laws at low temperatures (near the temperature when they are about to condense to a liquid) and at very high pressures (100 times atmospheric pressure).

Under normal conditions that we experience on earth, gases have close to ideal behavior.

Section 10-5: Dalton's Law of Partial Pressure

15) Sec 10-5.1 – Dalton's Law of Partial Pressures - 1801 (John Dalton, 1766-1844)

What happens if you combine non-reactive gases? The relationship was discovered by Dalton who determined that the total pressure exerted by a mixture of gases is the sum of their individual pressures. $P_{total} = P_a + P_b + P_c + \text{etc.}$

a) The partial pressure of a gas in mixture of gases is the pressure it would exert on the container if it were all alone in the same volume.

Example: What is the partial pressure of the oxygen in the atmosphere if the atmospheric pressure is 760 mm Hg and 20% of the air molecules are oxygen?

b) Collecting a Gas over Water – In the laboratory, many gases are collected by water displacement. This is an easy and reliable method.

If a volume measurement of the gas is made, this volume includes not only the gas being considered, but also water vapor. It then becomes necessary to make the proper allowance for this water vapor which is done by subtracting the vapor pressure that water exerts at that temperature from the total pressure that has been measured.

$$P_{gas} = P_{measured} - \text{v.p. of water}$$

The vapor pressure of water varies with the temperature of the water. (See water vapor table.)

Example: Suppose you prepared a sample of nitrogen and collected it over water at 15°C at a total pressure of 745 mm Hg. This sample occupied 310 mL. What would be the volume of the dry gas at STP?

Section 10-6: The Molar Volume and Density of a Gas

16) Sec 10-6.1 – The Molar Volume

The volume of one mole of any gas at STP is 22.4 L, and this is known at the **molar volume**. We have already used this relationship in Chapter 7 and proved it in the example above (and there is one in the book).

One mole of a gas is 22.4 L, 6.022×10^{23} molecules, and the molar mass. The first two just happen (remember the relationships in my bubble chart) and the third depends upon what the substance is.

Molar Mass of a Gas from Experimental Data

Since all gases have the same volume at a given temperature and pressure (for example 22.4L at STP), this fact can be used to determine the molar mass of any substance that is a gas or can be changed into a gas. $MM = \frac{mRT}{PV}$

Examples:

1) Calculate the molar mass of a gas if 0.840 g of the gas occupied a volume of 505 mL at 27°C and 740 mm Hg.

2) a) Calculate the empirical formula of a compound that contains 52.2% carbon, 13.0% hydrogen, and 34.8% oxygen.

b) Calculate the molar mass of the compound if 0.371 g of the compound when vaporized occupied a volume of 250 mL at 100°C and 750 mm Hg.

c) What is the molecular formula of the compound?

17) Sec 10-6.2 – The Density of a Gas at STP

In Chapter 3 we learned about the densities of solids and liquids, and that they had the units of g/mL. Gases, on the other hand, usually have the units of g/L (STP).

The densities are calculated by dividing the molar mass by the molar volume.

CO_2: 44.01 g/mol = 22.4 L/mol

$$\frac{44.01\ \text{g/mol}}{22.4\ \text{L/mol}} = 1.96\ \text{g/L (STP)}$$

Although gases have the same number of particles and the same volume, since they have different molar masses they will have different densities. A higher mass will have a higher density and *visa versa*.

Section 10-7: Stoichiometry Involving Gases

We have discussed stoichiometry using gases at STP. We merely converted the STP volume to moles and proceeded from there.

18) Stoichiometry Problems Involving Gases not at STP

Use $n = \frac{PV}{RT}$ to calculate the moles if the volume of a gas is given at other than STP.

Use $V = \frac{mRT}{P(MM)}$ to calculate the volume of a gas at conditions other than STP.

Examples:

1) How many grams of sodium are needed to react with 400 mL of chlorine at 25°C and 750 mm Hg? $2\ Na + Cl_2 \rightarrow 2\ NaCl$

2) What volume of carbon dioxide at a pressure of 5.0 atm and a temperature of 127°C will be produced by the reaction of 53 g of sodium carbonate with excess hydrochloric acid? $Na_2CO_3 + 2\ HCl \rightarrow 2\ NaCl + H_2O + CO_2$

19) Gay-Lussac's Law of Combining Volumes (not in book) – The volumes of different gases involved in a reaction, if measured at the same conditions, are in the same ratio as these coefficients for these gases in the balanced chemical equation.

Example: What volume of ammonia can be produced by the reaction of 200 mL of hydrogen with excess nitrogen? (All gases measured at room conditions.)

$N_2 + \_\_\_\_\_\ H_2 \rightarrow \_\_\_\_\_\ NH_3$