The mystics are the only ones who have gained a glimpse into what is possible.-Beatrice Hinkle

Gas Stoichiometry: Revisiting the Carbonate Project

Your data from previous experiments suggests that not only is mass conserved in a chemical reaction but also the *molar* ratio given in the balanced equation is observed as old compounds disappear and new compounds form.

If stoichiometry is to be of any practical use, it should be able to deal with reactions in which gases are involved too. In terms of practical work, however, the mass of gases produced in reactions on a laboratory scale is usually very small (less than 1 gram). However, the volume of these gases is generally large (more than say 20 mL). Thus the real problem is how to interpret *volume* data from the point of stoichiometry.

A common method of collecting gases in the laboratory is over water as you may have seen from your previous work. But in quantitative work this presents a complication. In addition to the gas collected there is also water vapor above the remaining water in the container used for displacement. This water vapor contributes to the total pressure of the gas sample and so to the total volume. Thus any method which depends upon pressure and volume to determine the amount of gas present must take the water vapor into account.

Recall that gases expand to fill their containers and that the total pressure of a gas sample is the sum of the partial pressures of the gases present (Dalton's Law) and consider the example below:

A 200.0 mL volume of methane is collected over water at a temperature of 298 K. The total pressure of the gas sample is 780.0 mmHg. At 298 K, the vapor pressure of water is 23.8 mmHg.

a) What is the pressure of the methane gas *only?*
b) How many moles of methane were collected?

To find the pressure of the methane, we invoke Dalton's Law:

$$P_T = P_{CH_4} + P_{H_2O}$$

$$780.0\text{ mmHg} = P_{CH_4} + 23.8\text{ mmHg}$$

$$\text{so } P_{CH_4} = \mathbf{756.2\ mmHg}$$

The *moles* of methane are easily found using the ideal gas law rearranged to solve for n:

$$\mathbf{n} = \frac{PV}{RT} = \frac{(756.2\text{ mmHg})(0.2000\text{ L})}{(62.4\text{mmHg} \times \text{L/mol} \times \text{K})(298\text{ K})} = \mathbf{0.00813\ mol}$$

This same principle applies whether a gas is contaminated by water vapor or some other gas. If the *volume* of a contaminating gas is known (measured at the same temperature and pressure) it can simply be subtracted from the total gas mixture volume and the correction done in that way rather than by partial pressure. <u>Both</u> of these methods are required in this experiment.

In **The Carbonate Project** earlier this year you used a variety of methods to determine the identity of your compound (Li_2CO_3, Na_2CO_3, K_2CO_3) by stoichiometric means. The first part of that experiment was the reaction of the compound with acid in an open container. We interpreted the mass change then as CO_2 lost, but what if you could *collect* the CO_2? Then the volume could be used to find moles if you knew the temperature and pressure. At that point the calculations would parallel those from the original experiment.

There is a problem with all this (beyond the various adjustments needed for contaminating water vapor and air): CO_2 is somewhat soluble in water! The soft drink industry is based on this happy circumstance but it causes problems for us in the context of the experiment. Be sure to take a close look at the technique section for a work-around to this problem.

Oh….the unknowns have been rescrambled!

Preparing to experiment

You will be provided with the following materials:

1. 3 M HCI (use about 5 mL)
2. 60 mL syringe w/cap and sample holder
3. an unknown alkali metal carbonate (use <u>**NO MORE**</u> than 0.15 g)

Design an experiment to collect and measure the carbon dioxide gas produced by the reaction of the alkali metal carbonate with HCl.

Adapted from “Percent composition of calcium carbonate in Tums®”, Bruce Mattson and Emily Saunders, CHEM 13 News, September 2003

Pre-lab take-home quiz

Answer these questions on a separate sheet of paper to be turned in on the day you do this experiment.

1. A certain volume of oxygen is collected over water which has a temperature of 20^oC. The total pressure of the gas mixture is 770.0 mmHg. The vapor pressure of water at 20^oC is 17.5 mmHg. What is the pressure of the dry oxygen?

2. An excess of HC1 is added to $CaCO_3$ and the following reaction occurs:

$$CaCO_3 + 2\ HC1 \rightarrow CO_2 + H_2\ O + CaCl_2$$

If 50.0 g of $CaCO_3$ is consumed, what volume of CO_2 will be formed (measured at 22^oC and 754 mmHg)? [R = 62.4 L·mmHg/mol·K]

3. The addition of a lump of sodium to water yields 3.45 L of hydrogen gas at STP. Assuming that water is in excess, how many grams of sodium reacted? *(hint:* you need to write a balanced equation!)

Technique

1. Preparing the sample

Small volumes of gases generated in the lab are often collected in a gas measuring tube which is like a very large graduated cylinder except that it is used with the open end pointed down and the 0.0 mL mark is at the closed end on top. The gas to be collected is either bubbled into the tube, displacing water, or--as in this experiment--the reaction may take place *within* the lower portion of the tube, displacing water as it does.

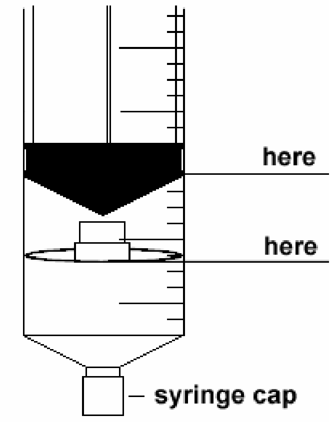
The new microscale technique used in this experiment uses a 60 mL syringe as both a reaction and collection vessel. Successful completion of the experiment requires careful technique and very little deviation from the series of steps that follow.

The carbonate sample is first measured into the small plastic vial cap that serves as a sample holder. Very little is needed [too much and the syringe will pop open!] and the “shoveling” process can get messy, so be careful at the balance.

Next the sample is placed in the syringe. This is done by filling the syringe with tap water while keeping a finger over the hole at the other end. Then the vial cap with the sample in it is carefully floated on the water. Removing the finger allows the water to drain and the sample slowly descends to the bottom. It is important that the sample not get wet at this point, so be sure to hold the syringe vertical and don’t slosh the water around on its way out.

The plunger is now carefully inserted and pressed all the way down, trapping the sample. There is a slight “stop” near the mouth of the syringe when the plunger is first inserted and you need to be careful not to upset the sample when you press the plunger past this point.

2. Reactions in the syringe



5 mL of the HCl is carefully drawn up into the syringe (keep it vertical!!!). Place the syringe cap firmly over the end and hold the syringe at eye level to read *both* the HCl level *and* level of the syringe plunger. The difference gives the initial volume of air in the syringe.

Gently but thoroughly shaking the syringe allows the sample to react with the acid and the plunger should slowly move outward.

The next series of steps insures that very little CO_2 remains dissolved in the acid solution and that the pressure of the gas mixture (CO_2, air, water vapor) is essentially the same as the room pressure.

Pull out and hold the plunger an additional 5 mL and shake the syringe vigorously, tapping the sides with your hand. The agitation helps force dissolved gas out of solution (just like shaking a soda). Immediately place the end of the syringe under water and—still holding the plunger out—remove the end cap. Some water should rush in to equalize the pressure. Replace the end cap while the syringe end is still under water and take care not to change the position of the plunger.

Hold the syringe vertical and at eye level again and read both the liquid level and the level of the syringe plunger once again. The difference gives the volume of the final gas mixture (which includes the air from the initial measurement).

The experiment can and should be repeated. The only part that must be dry before you can do the whole thing again is the little sample cap.

Analysis

1. Write a balanced molecular equation for the reaction between the carbonate "X_2CO_3" and hydrochloric acid.

2. Correct the final volume of gas for the volume of air that was present before the reaction began.

3. Using the vapor pressure table for water below and your data, correct the total pressure for the contaminating water vapor.

Vapor Pressure of Water		
Temperature, ^{o}C	Pressure, mmHg	Pressure, kPa
17	14.5	1.93
18	15.5	2.07
19	16.5	2.2
20	17.5	2.33
21	18.7	2.49
22	19.8	2.64
23	21.1	2.81
24	22.4	2.99
25	23.8	3.17
26	25.2	3.36
27	26.7	3.56
28	28.3	3.77

4. Use your data and the answer to #3 to calculate the moles of CO_2 collected.

5. Based on the balanced equation in #1, determine the moles of X_2CO_3 and the identity of "X" [stuck???? look back at the Carbonate Project!]

6. Knowing the identity of the carbonate, show that the HCl used in the experiment was in excess.

7. Determine the theoretical volume of CO_2 that should have been collected at the same temperature and pressure and calculate the % error.

8. Repeat these calculations for your second trial [you do not need to show all the details for these repeat calculations].