> Results! Why, man, I have gotten a lot of results. I know several thousand things that won't work.
> --Thomas A. Edison

The Carbonate Project

By now you have a good feeling for what a chemical reaction looks like. But in addition to the information that is contained in the *appearances* of a chemical process, there is information in the *quantities* of a chemical process. In the determination of empirical formulae you have seen that reacting masses are important (and fixed). The ratios in which substances combine in a chemical reaction may be measured by mass, but it is most convenient to express them in terms of moles since in that we are "counting" the atoms as they rearrange. Thus in your determination of the empirical formula for zinc iodide you eventually reduced all of your mass data to a ratio of moles zinc/moles iodine.

The reaction of an alkali metal carbonate (Na_2CO_3 for example) with nitric acid is an interesting system to look at because it is simple and yet versatile. The quantitative relationships (or the *stoichiometry*) involved in the reaction can be examined from several different viewpoints. For example, when the acid reacts with the carbonate, all of the CO_3^{2-} is converted to CO_2. If the gas is allowed to escape, the mass of CO_2 lost contains valuable information about the ratio of HNO_3 added to the amount of metal carbonate originally present.

The soluble alkali metal carbonate can also be converted to an *in*soluble carbonate and the moles of that solid will be related to the moles of the starting material.

In this experiment we will also introduce the concept of *solution stoichiometry*, that is, the idea that a volume of solution can be used to measure the amount of dissolved material added just as a mass measurement can. This is true, of course, only if the concentration of the solution is known. We conveniently express concentration in **moles/Litre** or **Molarity** (**M**) because moles are the fundamental measuring units in chemical processes.

Finally, the reaction of HNO_3 with the original compound can be followed more closely as an acid/base titration (carbonate solutions are slightly basic) using an indicator. This final method brings all techniques together: masses and volumes are used to determine the amount of the metal carbonate.

Adapted from: <u>A Carbonate Project Introducing Students to the Chemistry Lab</u>, Emily Dudek, *J. Chem. Educ.*, 1991, v. 68, p. 948

As described, the planned "experiment" is pretty much another exercise. To make this exercise a little more sporting, we will add a slight twist. There are five alkali metals, all of which form stable carbonates with the general formula **X_2CO_3**. The latter two (Rb_2CO_3 and Cs_2CO_3) are very expensive, but the first three are quite common in the lab. Your goal in this experiment is to use the data you collect from the three procedures to determine which of the first three possible carbonates you have been given!

Note that in each procedure as generally described you can determine the moles of CO_3^{2-} in your sample. According to the formula, the moles of **X** are in a 2:1 ratio with this value. The *mass* of that number of moles of **X** can be determined by difference if you know the mass of CO_3^{2-} lost or reacted. And the mass/mole of **X** should agree with the atomic mass of one of the first three alkali metals.

| Preparing to experiment |

You will be provided with the following materials:

1. an unknown alkali metal carbonate
   (use about 2 g in the first procedure, about 1 g in the second and about 0.10 g in the third)
2. 6 M HNO_3 (that's 6 moles HNO_3/Litre)
   (use about 25 mL in the first procedure)
3. 0.20 M $CaCl_2$ solution
   (use about 80 mL in the second procedure)
4. 0.10 M HNO_3 (use for the titration)
5. methyl orange/indigo carmine mixed indicator (use about 5 drops)
6. filter paper circles
7. a 600 mL beaker
8. a 50 mL buret
9. a magnetic stirrer

Design an experiment in which the mass loss of a sample of alkali metal carbonate is determined after reaction with acid in a 250 mL erlenmeyer flask. Remember that an immediate goal is to limit the loss of material, and spray will be generated when the acid comes in contact with the solid.

Design an experiment by which you can determine the mass of calcium carbonate formed when a solution of alkali metal carbonate (use <u>up to</u> 300 mL of distilled water to get your sample to dissolve) is mixed with a solution of calcium chloride.

Design an experiment by which you can accurately measure the amount of HNO_3 needed to "neutralize" a sample of an alkali metal carbonate using an indicator.

Answer these questions on a separate sheet of paper to be turned in on the day you do this experiment. **Note that these three questions are based on the three different experimental techniques. Because of scheduling, you may not do the experiment in the same order in which it is written. Each night you should only do the question below that is pertinent to the work you will do in the lab on the following day.**

1. A sample of 1.60 g of X_2CO_3 is dissolved in excess nitric acid and all of the resulting CO_2 expelled. The added mass of acid is 26.10 g. The final mass of the solution mixture is 26.75 g.
a. How many grams of CO_2 were lost?
b. How many moles of CO_2 is this?
c. How many moles of X_2CO_3 must have been present (each X_2CO_3 makes one CO_2)
d. Based on your answer to (c) and the starting mass of the sample, what is the approximate molar mass of unknown carbonate?
e. Subtracting the molar mass of CO_3^{2-} from the answer to (d) and dividing by 2 should give an approximate atomic mass for X. Do this and SHOW WHY THIS IS TRUE.

2. A 0.75 g sample of X_2CO_3 is dissolved in water and 80 mL of 0.20 M $CaCl_2$ solution is added.
a. Write a balanced molecular equation for the reaction that takes place.
b. If the mass of dried, washed precipitate is 0.71 g, calculate the moles of $CaCO_3$ formed.
c. Based on the ratio in your balanced equation, how many moles of X_2CO_3 must have reacted? How many moles of CO_3^{2-} is this?
d. Find the approximate molar mass of X_2CO_3 from the initial sample mass and the moles in (c).
e. Perform an operation similar to that described in (1.e) to get the approximate atomic mass of X.
f. As an afterthought, calculate the moles of $CaCl_2$ in the 80.0 mL of 0.20 M $CaCl_2$. How many moles of Ca^{2+} does this provide?
g. Show that the amount of $CaCl_2$ in (f) provides more Ca^{2+} than is needed to react with all the CO_3^{2-} present and form a precipitate

3. The reaction of HNO_3 with X_2CO_3 produces CO_2, water, and XNO_3.
a. Write a balanced molecular reaction for this process.
b. If 17.4 mL of 0.10 M HNO_3 was required to "neutralize" a 0.12 g sample of X_2CO_3, how many moles of HNO_3 is this?
c. Based on your balanced equation, how many moles of X_2CO_3 must have reacted with the moles of HNO_3 in (b)?
d. Use the sample mass and moles in (c) to calculate an approximate molar mass for X_2CO_3.
e. Determine an approximate atomic mass for X using this information (see 1.e)
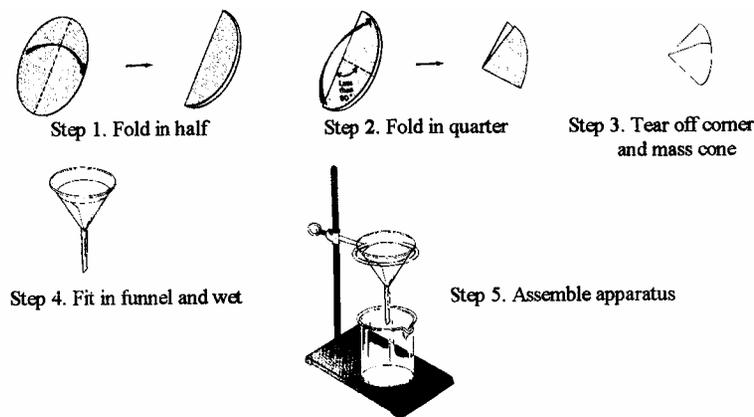
1. Digesting a precipitate

Frequently precipitates form in solution as very fine crystals that will pass through filter paper, yielding poor results. Such is the case with calcium carbonate. This effect can be minimized by "digesting" the precipitate, helping larger crystals to form. Usually this is done by heating the mixture (in this case, just to boiling) and then allowing it to cool somewhat before filtering. If the digestion is complete and the filter paper is prepared properly, the filtrate should be clear and free of solid.

2. Filtering

Gravity filtration is a somewhat slow process for separating precipitates from mixtures, particularly those which tend to remain suspended. A circular piece of paper is folded as shown in the diagrams below and then opened into a cone. This cone is fitted into a funnel. A container under the funnel catches the liquid (called the *filtrate*) and the solid (the *residue*) is caught in the paper.

For quantitative work, the paper cone should be prepared and **massed** before fitting it into the funnel. Then the cone is held in place in the funnel by adding a small amount of solvent (generally water) with an eyedropper or wash bottle. It should fit smoothly on all sides.

Step 1. Fold in half   Step 2. Fold in quarter   Step 3. Tear off corner and mass cone

Step 4. Fit in funnel and wet   Step 5. Assemble apparatus

3. Titration

You already know the essentials of titration. But the **buret** is the commonly used volumetric glassware for this procedure. It is graduated in 0.1 mL intervals, like a long graduated cylinder, but more accurate. It has a valve at the bottom for letting the solution out in measured amounts, from a slow drip to a steady stream.

The solution to be titrated is placed in a beaker or flask under the filled buret. Indicator is generally added. The mixture should be stirred as the titrant is added. This can be done by hand or a device called a magnetic stirrer can be used. This is a motor with a magnet attached to its shaft mounted under a platform . A small teflon-coated magnet is placed inside the beaker or flask and when the motor turns, the magnet follows it. Mixing insures that the reaction will be complete as the titrant is added.

At the beginning of a titration you can generally go pretty fast, but you should slow down when you notice a color change occurring around where the titrant is dripping in, finally going drop-by-drop to get the exact point at which the color changes. In this experiment, the indicator changes from green to purple.

A buret should always be rinsed thoroughly after use and clamped upside down with the valve open so that the entire body will drain.

4. Massing for transfer

Whenever substances must be quantitatively transferred (i.e., transferred without loss) you need to think carefully about how you measure. The general rule is to *choose a procedure that minimizes transfer*. For example, in the first method when you need to know the total mass of the mixture before reaction and the total mass after reaction, you should be careful how you measure the added HNO_3, remembering that not all of it will pour out of the graduated cylinder and into the flask (some will cling to the sides of the cylinder). Thinking about these kinds of operations before you do them will ensure that you record sufficient data so that you will be able to interpret your results later.

_____

The chemicals

Lithium carbonate, sodium carbonate and potassium carbonate are the possible compounds you might have in this experiment. All are relatively hygroscopic, but K_2CO_3 is the worst. So they are stored in the oven or a desiccator when not in use. Lithium carbonate is used in pottery glazes and for treatment of manic psychosis. Dry sodium carbonate, sometimes called *soda ash*, is a white powder with a bitter taste. The hydrated form is sometimes called *sal soda* or "washing soda" and is still used in some laundry detergents and as a general cleanser. Potassium carbonate is used in the manufacture of some soaps and glasses as well as for tanning leather.

Calcium chloride is obtained as a by-product in the manufacture of sodium carbonate (The Solvay process). It is *very* hygroscopic and the anhydrous form is used as a drying agent. It is also useful for fireproofing fabrics, for melting ice and snow on the ground and roads, in concrete mixtures for greater strength, and as a brine for filling inflatable tires on tractors to provide better traction.

Methyl orange is a complex hydrocarbon which is used as an indicator for combinations of weak bases and strong acids. It changes from red to yellow as the acidity of a solution decreases.

Indigo carmine is another complex hydrocarbon which is sensitive to the amount of acid or base in a mixture. It has been used as a food dye (FD & C Blue #2) as well as a general purpose dye. It is yellow in strongly basic solutions and blue in less basic solutions.

Analysis

These questions should be answered in your laboratory notebook, following your data and observations.

1. Use your data from the mass loss of CO_2 to determine a value for the atomic mass of the metal **X** in your carbonate unknown and make a tentative identification of the metal. Discuss any variation in the mass you calculate and the known atomic mass of the metal you choose (e.g., would you expect your value to be high or low, etc.).

2. Use your data from the precipitation of $CaCO_3$ to determine a second value for the atomic mass of **X**. Discuss any variation in the mass you calculate and the known atomic mass of the metal you choose (e.g., would you expect your value to be high or low, etc.).

3. Use your titration data to determine a third value for the atomic mass of **X**. Discuss any variation in the mass you calculate and the known atomic mass of the metal you choose (e.g., would you expect your value to be high or low, etc.).

When you have completed all three parts and the flame test (next page) decide which unknown carbonate you had and explain your choice briefly.

An afterthought:

The alkali metals are known for the brilliant and distinctive colors they give to a burner flame when their compounds are injected. According to the Handbook of Chemistry and Physics, these are the colors:

> Lithium: deep red or reddish-purple
> Sodium: bright yellow or yellow-orange
> Potassium: pale lavender

Go back to the lab to check your result!

To do a flame test, dissolve a speck of the unknown in 1 mL or less of 6 M HCl. Dip a wire loop into a small amount of 6 M HCl and hold it in the flame. Repeat this until there is no color added to the flame before the wire itself becomes red-hot. Now dip the wire into the solution you made and place it in the flame again. Repeat this several times until you can identify the color.

Congratulations! You have just completed a very challenging set of experiments!