Experiment 6D

FV 9/16/04

A SERIES OF REACTIONS INVOLVING COPPER

MATERIALS: copper turnings, scissors, 6.0 M nitric acid, copper nitrate, sodium carbonate monohydrate, 3.0 M sulfuric acid, 95% ethanol, steel wool, evaporating dish, 11 cm watch glasses, 250 mL beaker, 400 mL beaker, thermometer, gravity filter funnel, Buchner funnel, filter paper, suction flask, rubber hose, microscope, 50 mL volumetric flask and stopper, 50 mL graduated cylinder, weighing dish, 100 mL beaker, 150 mL beaker

PURPOSE: The purpose of this experiment is (1) to illustrate both quantitative and qualitative aspects of several types of chemical reactions, including oxidation/reduction reactions and precipitation reactions, and (2) to introduce the use of various types of chemical equipment and techniques.

LEARNING OBJECTIVES:

1. Write balanced reactions, including net ionic equations, for a given chemical transformation.
2. Using balanced reactions, determine the mass of reactants or volume of solutions containing reactants required for complete reaction.
3. Calculate the theoretical and actual yields for a chemical reaction.
4. Correctly make an aqueous solution of specified concentration.

DISCUSSION:

In this experiment, copper metal will react in a series of steps, represented symbolically as follows:

$$Cu\ (s) \rightarrow Cu(NO_3)_2\ (aq) \rightarrow Cu_2CO_3(OH)_2\ (s) \rightarrow CuSO_4{\cdot}5H_2O\ (s) \rightarrow Cu\ (s) \qquad (1)$$

Each individual step represents a chemical reaction, without showing all of the details. For example, for the first reaction, the more complete representation is

$$Cu\ (s) + 4\ HNO_3\ (aq) \rightarrow Cu(NO_3)_2\ (aq) + 2\ NO_2\ (g) + 2\ H_2O\ (l) \qquad (2)$$

This is an example of an oxidation/reduction reaction. Solids, liquids, gases, and solutions are carefully denoted by the parenthesized notations. The balanced reaction provides the necessary information for determining the amounts of reactants required, and for predicting the amounts of products which could be produced.

In order to proceed through the steps of a series of reactions, it is sometimes necessary to isolate the relevant product from the preceding step so that it can serve as one of the reactants in the next step. For example, the compound $Cu_2CO_3(OH)_2$ (s) is formed in the second step as a precipitate from a mixture of aqueous solutions. It can be separated from this liquid solution through filtration and drying, and then used as a reactant in the third step.

In a multi-step process such as this, it may be possible to determine the percentage of the original reactant (i.e., copper metal) which has been successfully transformed and incorporated into products in later steps. Less than 100% successful transformation may result (1) if reactions do not proceed to completion, (2) if alternate products (side products) form, or (3) if certain experimental

procedures inherently result in loss of materials. The actual amount of product recovered will always be less than or equal to the maximum theoretical amount which is based solely on the balanced reactions. The % yield is the ratio of these two quantities, multiplied by 100%.

Unique carbonate chemistry. The second step in the series involves carbonate ions, which exhibit interesting properties when involved in certain reactions. For example,

$$CO_3^{2-}\,(aq) + 2\,H^+\,(aq) \rightarrow H_2CO_3\,(aq) \qquad (3)$$

Carbonic acid is unique because of its strong tendency to dissociate into carbon dioxide gas and water, i.e.,

$$H_2CO_3\,(aq) \rightarrow CO_2\,(g) + H_2O\,(l) \qquad (4)$$

Thus, adding carbonate ion to acid will produce significant effervescence due to the carbon dioxide gas.

Even when not in the presence of acid, carbonate ions often react in unexpected ways. For example, one might expect that the second step of the series, which involves simply mixing copper (II) ions with carbonate ions, would yield copper (II) carbonate solid:

$$Cu^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightarrow CuCO_3\,(s) \qquad (5)$$

If this represented the actual reaction, there would be no observed effervescence. This is not the case, however, as will be proven during this experiment. Though the explanation for this reaction is beyond the scope of a general chemistry course, the actual reaction produces carbonic acid, H_2CO_3 (aq), which in turns dissociates into carbon dioxide and water, and a complicated copper carbonate compound, $Cu_2CO_3(OH)_2$, known as *malachite*:

$$2\,Cu^{2+}\,(aq) + 2\,CO_3^{2-}\,(aq) + 2\,H_2O\,(l) \rightarrow Cu_2CO_3(OH)_2\,(s) + H_2CO_3\,(aq) \qquad (6)$$

Careful observations and mass measurements will verify that this is the actual reaction.

PROCEDURE:

First Laboratory Period:

1. Find the MSDS for nitrogen dioxide gas, which is a product of the first step of the series of reactions (see equation 2 above). Determine if there are any health hazards and any recommended steps for controlling this gas.

2. Observe the experimental procedures demonstrated by your instructor, including gravity filtration, vacuum filtration and the double-boiler. Make any special notes for future reference.

3. Starting with about 0.5 g Cu, determine the volume of 6.0 M HNO_3 required for complete reaction, using the correct balanced reaction. Carry out this reaction in an evaporating dish covered with a watch glass, in the hood, as demonstrated by your instructor. Use an excess (at least 20%) of the acid solution. Calculate the amount of all species remaining in the solution to at least two significant figures. *Set this solution aside until step 5 below.*

4. Dissolve a small amount of copper (II) nitrate in water in a small beaker. This solution is similar to that prepared in step 3 above, except that there is no excess acid present. Now dissolve a small amount of sodium carbonate in another small beaker. Mix the two solutions together. Based on your observation of the resulting changes, decide whether reaction 5 or 6 has occurred. Why would your observation be *inconclusive* if excess acid had been present?

5. Determine the mass of Na_2CO_3 needed to completely react with the excess acid and with Cu^{2+} ions produced in step 3 above. Using a volumetric flask, make 50 mL of a solution containing at least a 25% excess of CO_3^{2-}. Mix the solution from step 3 and the sodium carbonate solution in a 250 mL beaker, making sure that all of the Cu^{2+} containing solution has been transferred from the evaporating dish. Carefully warm the resulting blue-colored solution with a double-boiler system to between 55°C and 60°C. If the temperature goes much above 60°C, the copper carbonate compound begins to decompose, producing unwanted copper (II) oxide, i.e.,

$$Cu_2CO_3(OH)_2\ (s) \rightarrow 2\ CuO\ (s) + H_2CO_3\ (aq) \qquad (7)$$

Keep the solution in this temperature range until the sky blue color changes to a light green. As soon as this transition occurs, remove the 250 mL beaker from the double boiler setup and allow the solution to cool for several minutes to room temperature. Using a gravity funnel filter, as demonstrated by your instructor, collect the solid on a pre-weighed filter paper. Transfer as much of the green compound as possible to the filter paper. You should use water to rinse the beaker several times. This also ensures that any excess sodium carbonate has been flushed out of the solid and passed through the filter paper. Set the wet filter paper containing the green compound in a plastic beaker with your name on it, as indicated by your instructor, and set aside until the next laboratory period. This will allow sufficient time for the sludgy material and filter paper to completely dry.

Second Laboratory Period

The dried green copper carbonate compound is known as *malachite*. Carefully measure the mass of malachite obtained. Using this mass, verify that the solid obtained in this step is not the simple $CuCO_3$, as might have been expected initially. Report the mass of copper turnings and the mass of malachite to your instructor for later use by the entire class.

6. Determine the volume of 3.0 M H_2SO_4 needed to completely react with the $Cu_2CO_3(OH)_2$, based on the correct balanced reaction. As best you can, remove the dried malachite from the filter paper and place in a 150-mL beaker. Add the determined amount (plus a slight excess) of sulfuric acid. After all the solid is dissolved and cooled to room temperature, add about 40 mL of ethanol. Gently stir the mixture with a glass rod until the soft needle-shaped crystals of copper sulfate pentahydrate begin to form. Allow the crystals to form for a few minutes without stirring. Using a Buchner funnel filter and vacuum filtration system, collect the solid on a pre-weighed filter paper. After aspirating the solid for a few minutes, carefully measure the mass of the solid and paper. Carefully observe a few of the copper sulfate pentahydrate crystals through a microscope, making a rough sketch in your laboratory notebook.

7. From the masses of the malachite and the copper(II) sulfate pentahydrate obtained, determine the percent yield after steps 2 and 3 of the reaction series.

8. Dissolve the copper(II) sulfate pentahydrate crystals in water in a small beaker. Place a rolled up ball of steel wool in the beaker and observe any changes that occur. Explain whether your observations are consistent with the following reaction:

$$Fe\ (s) + Cu^{2+}\ (aq) \rightarrow Fe^{2+}\ (aq) + Cu\ (s) \qquad (8)$$

QUESTIONS FOR CONSIDERATION:

1. What would it mean if the liquid solution above the malachite in step 5 had been slightly blue?

2. Assuming the product of the second step is $CuCO_3$, how many grams would have been obtained, assuming 100% reaction and no loss of material? Do the same calculation, assuming the product of the second step is malachite, $Cu_2CO_3(OH)_2$. Does your data better support one of these assumptions? Is this consistent with your observation when copper ions were mixed with carbonate ions? Explain.

3. The sky blue colored precipitate initially observed upon adding sodium carbonate solution to the copper(II) solution obtained after step 1 is actually different than the final light green malachite compound. It is known as *azurite* and has the chemical formula $Cu_3(CO_3)_2(OH)_2$. How many grams of azurite would you expect to obtain, assuming 100% yield, based on the original number of grams of Cu?

4. Find information relating to the copper compounds azurite and malachite. What are they typically used for? How have paintings been affected by the same transition you saw between the two compounds?

5. What is the balanced reaction for the third step of the series?

6. Why do the copper(II) sulfate pentahydrate crystals form when ethanol is added?

7. Write the net ionic equation for each of the steps of this series of reactions.

8. Use the class data to verify that the product of the second step is, in fact, not the simple compound $CuCO_3$. Do this by determining the mean and standard deviation from the mean, and comparing to the value expected if the product were $CuCO_3$.

9. The mass of the copper(II) sulfate pentahydrate may have led to an unrealistic percent yield. Given the procedures followed, why might this be so?

10. Based on your observations in step 8, what color do solutions containing Cu(II) ions typically have? What color do solutions containing Fe(II) ions typically have?

11. Identify the oxidation numbers for all species in the reactions of steps 1 and 2. Use this information to help distinguish between oxidation/reduction reactions and precipitation reactions.