# Experiments

## EXPERIMENT 6
## Copper reactions

### 6.1. Safety

Aqueous nitric acid and aqueous sulfuric acid are hazardous. They produce severe burns on the skin and the vapor is a lung irritant. These compounds should be handled in a fume hood. Rinse your hands with water for 5 minutes after handling the acid bottles. The gases produced during these reactions are toxic and must be avoided. Thus, when the experiment states that a procedure should be performed in the fume hood, DO so. Aqueous sodium hydroxide is also corrosive to the skin and is especially dangerous if splashed into eyes. Copper sulfate pentahydrate is harmful if swallowed and can cause irritation to skin, eyes and respiratory tract. At high concentrations, this compound can affect the liver and kidneys. If any of this compound comes in contact with the skin or the eyes, flush with copious amounts of water. Methanol is flammable and should never be heated over an open flame. Bunsen burners, hot glassware, and metal ring stands can cause painful and serious burns to skin.

**Before Laboratory Questions**
*These questions should be used to help you write your notebook and should be answered in some form before you go to the laboratory.*

(1) What is the purpose of this experiments?
(2) What is the copper cycle? Answer in a single if/then statement.
(3) Write the balanced chemical reactions for each step in the cycle.
(4) What materials are required for this experiment? Are any chemicals needed? If so, what are they? Which materials must be obtained from the stockroom, which must be obtained from the instructor, and which are in your laboratory drawer?
(5) What are the steps for each reaction in the cycle?
(6) Create a space to record the initial mass of copper and the final mass copper.
(7) Create a table that allows you to write your observations for each step in the reaction cycle. Be sure to record the color of any precipitates and gases created during this experiment.

## 6.2. Introduction

We have now investigated precipitation reactions (either double displacement or single displacement), acid/base reactions, decomposition reactions and oxidation/reducation reactions. In this experiment, you will use the skills obtained from the previous experiment to study a cyclical reaction series.

## 6.3. Experiment 6. The copper cycle

### 6.3.1. Reaction 1

**REACTION 1 MUST BE PERFORMED IN THE FUME HOOD SINCE IT GENERATES A VERY TOXIC, NOXIOUS GAS AS A PRODUCT.**

The first reaction in this cycle is the reaction of solid copper with nitric acid to generate aqueous copper nitrate and gaseous nitrogen dioxide. Initially, weigh a test tube. (The instructor will inform you of the test tube size during pre-laboratory.) Then, place approximately 0.1 - 0.2 g of copper metal (From Experiment 4) into the test tube and weigh it again. Record the mass of copper on the Report Sheet. **In the fume hood**, add 2 mL of 6 M nitric acid. Warm the contents in a hot water bath, if necessary. Heat until all of the copper has dissolved and no more nitrogen dioxide (a red/brown gas) is produced. Once the reaction is complete, return to your laboratory bench with the test tube containing the reaction mixture. Record your observations in your laboratory notebook.

### 6.3.2. Reaction 2

The second reaction is the reaction of aqueous copper nitrate with aqueous sodium hydroxide to generate solid copper hydroxide and an aqueous salt. To perform this reaction, add 6 M sodium hydroxide solution dropwise until the solution is basic. Stir well with a stirring rod after the addition of each drop. You can test the pH of the solution by touching the stirring rod to red litmus paper. If the paper turns blue, the solution is basic. However, do not mistake the blue precipitate with the litmus paper reaction. Record your observations in the laboratory notebook.

### 6.3.3. Reaction 3

The third reaction in the cycle is the decomposition of copper hydroxide to copper oxide. This transformation is achieved by gently heating the test tube in a hot water bath until the chemical reaction is complete. Allow the solution to cool to room temperature without the use of an ice bath. Once cool, centrifuge the tube. Discard the supernatant into a beaker using a pipette and keep the solid. (Remember to balance the centrifuge with a similar tube containing approximately the same volume of liquid placed 180° from your test tube.) Wash the solid twice. For each wash, add 2 mL of deionized water, swirl the test tube, centrifuge and decant. Record your observations.

### 6.3.4. Reaction 4

The formation of aqueous copper sulfate from copper oxide and sulfuric acid is the fourth reaction in the copper cycle. Weigh a small clean, dry beaker. Then place 6 mL of 3 M sulfuric acid into the beaker. Use a spatula to transfer the solid from Reaction 3 into the beaker. You can rinse the test tube with a small amount of the 3 M sulfuric acid and then with $1-2$ mL of distilled water. All liquid should be placed into the small beaker. Record your observations.

### 6.3.5. Reaction 5

The final reaction is the reaction of the aqueous copper sulfate with magnesium to generate copper and aqueous magnesium sulfate. Cut a long (20 cm) length of magnesium ribbon. Polish the ribbon with steel wool until it is shiny and cut the ribbon into 1 cm lengths. Add 5 mL of deionized water to the reaction solution from Reaction 4 and swirl gently to mix. Then, add the 1 cm magnesium ribbon lengths one at a time and observe. Keep adding strips until the solution is colorless. If a white, milky precipitate forms [$Mg(OH)_2$], add several drops of 6 M sulfuric acid to dissolve the magnesium hydroxide.

Once the solution is colorless, take a small drop of solution and transfer it to a small test tube. Add approximately 0.5 mL of water and a few drops of concentrated ammonia to the drop in the small test tube. If there are traces of copper ion in solution, the copper ion will complex with the ammonia to form a deep blue complex. If this deep color is observed in the test tube, add another magnesium strip to the beaker.

When you no longer obtain a positive test for copper ions, stop adding magnesium. With a stirring rod, break up the red-brown coating on the magnesium ribbon. Decant as much water as possible without losing product. Then add 6 M sulfuric acid dropwise until the excess magnesium is gone. After each drop of sulfuric acid, break up the solid pieces using your stirring rod. Continue adding sulfuric acid until no evidence of a reaction is observed. Decant the liquid. Rinse the copper with two rinses of methanol and dry on a hot plate (or over a hot water bath). Dry the outside of the beaker and weigh to determine the mass of the copper solid. **If time permits, you should perform the complete reaction cycle a second time.**

**After Laboratory Questions**

*These questions should be used to help you write your notebook and should be answered in some form after completion of the laboratory.*

(1) The percent yield gives the percent difference between the expected yield $m_t$ of a chemical reaction and the actual yield $m_a$ of the same reaction. This yield, which can be written as

$$\% \text{ yield } = \frac{m_a}{m_t} \times 100 \,, \tag{6.1}$$

is rarely 100% due to errors (both systematic and random). Calculate the theoretical yield of the copper-containing product of each step based on your initial mass of copper. Then, calculate the % yield.

(2) Discuss what types of systematic error could have led to a % yield $\neq$ 100. (A systematic error is a consistent and repeatable error such as the error in the measurement of mass on an electronic balance or the error in reading the volume of a graduated piece of glassware.)

(3) Discuss what types of random error could have led to a % yield $\neq$ 100. (Random errors arise from random fluctuations such as the transfer of precipitate from a stirring rod to a piece of litmus paper.)

(4) In the last step, why did the sulfuric acid react with the magnesium and not the copper?

(5) Why does sulfuric acid not dissolve copper (Reaction 5), but nitric acid does (Reaction 1)?

(6) Identify each reaction as a precipitation reaction, a oxidation/reduction reaction, a decomposition reaction, or an acid-base neutralization reaction. (Note: For this course, an acid-base neutralization reaction always yields a soluble or insoluble salt and water.)

## 6.4. Reminders

Remember to get your results signed before leaving the laboratory and to submit your laboratory notebook pages.

## 6.5. Practice problems

The problems below are excellent practice problems for the laboratory quiz and the laboratory practical. Since these problems will not be graded, the answers are given in Appendix I.

(1) A mixture of CuO and $Cu_2O$ with a mass of 10.50 g is reduced to give 8.66 g of pure Cu metal. What are the amounts (in grams) of CuO and $Cu_2O$ in the original mixture?

(2) If 3.42 g of potassium platinum(II) chloride and 1.61 g of ammonia give 2.08 g of cisplatin (i.e., $Pt(NH_3)_2Cl_2$), what is the percent yield of the reaction? (Note: Potassium chloride is the other product of this reaction.)

(3) If the reaction to form cisplatin (see Problem 2) takes place with a 75% yield, how much starting material would you need to generate 6.75 g of cisplatin? If potassium platinum(II) chloride is \$287.00 for each 5 gram amount and \$72.30 for each 1 gram amount and $NH_3$ is \$435 for 170 g, what is the cost of this experiment when only the minimal amount of chemicals are purchased? (Note: The prices given are for the smallest quantities that can be purchased. The cost should be quoted to the nearest dollar.)

(4) Brass is an approximately 4:1 alloy of copper and zinc along with small amounts of tin, lead and iron. Different alloys of brass have different properties and, therefore, brass is graded on the exact mass percentage of copper and zinc in the alloy. Thus, each new lot of brass must be tested to determine the exact alloy that was prepared. This test is performed by:
Step 1: Dissolve the brass in hot nitric acid to generate aqueous copper(II) and zinc (II) and nitrogen oxide. The acidity of the solution is then adjusted to go to the next step.
Step 2: Sulfurous acid (i.e., $H_2SO_3$) is added to the solution to convert copper(II) to copper(I), while generating sulfate ions. The copper(I) is instantly precipitated as copper(I) thiocyanate by the addition of sodium thiocyanate (i.e., NaSCN). The zinc(II) does not react in this step.
Step 3: The solid copper thiocyanate is removed by filtration and the filtrate (i.e., liquid remaining after filtration) is kept. (The acidity of the filtrate is adjusted to neutral.) Step 4: A solution of diammonium hydrogen phosphate (i.e., $(NH_4)_2HPO_4$) is added to the aqueous zinc(II) solution to give a precipitate of zinc ammonium phosphate (i.e., $ZnNH_4PO_4$). Step 5: The zinc ammonium phosphate precipitate is heated to 900°C to convert it to zinc pyrophosphate (i.e., $Zn_2P_2O_7$), which is weighed. This reaction releases gas phase ammonia and gas phase water. Step 6: The copper thiocyanate is dissolved in aqueous acid to give copper(I) and thiocyanate ions. This solution is then treated with potassium iodate to give aqueous iodine and copper(II). Step 7: The amount of copper(II) in solution is determined indirectly by measuring the amount of aqueous iodine in solution using a technique called titration. The aqueous iodine is reacted with aqueous sodium thiosulfate to give aqueous iodide and aqueous tetrathionate (i.e., $S_4O_6^{2-}$).
   (a) Write the balanced chemical reactions for Step 1, Step 2, Step 4, Step 5, Step 6, and Step 7.

(b) When a brass sample with a mass of 0.636 g was subjected to the above analysis, 10.83 mL of 0.1220 M sodium thiosulfate was required to convert all of the aqueous iodine to aqueous iodide in Step 7. What is the mass percent of copper in the brass?

(c) The brass sample in (b) yielded 0.496 g of $Zn_2P_2O_7$. What is the mass percent zinc in the brass?

(d) What alloy of brass is this sample? [Alloy 260: 70.0% Cu and 30.0% Zn; Alloy 272: 63.5% Cu and 39.5% Zn; Alloy 330: 66.0% Cu and 33.5% Zn; Alloy 353: 61.5% Cu and 36.5% Zn; Alloy 360: 61.5% Cu and 35.4% Zn; and Alloy 464: 60.0% Cu and 39.3% Zn]

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