INS Chemistry Lab for weeks 5 and 6, Fall 2007
Reactions of Copper

Suggested Reading: Chemistry text sections 4.1-4.4

Introduction

This lab is designed to demonstrate a range of types of chemical reactions. Copper metal will be converted into copper ions, put into and out of solution, and eventually be recovered as copper metal. Copper is an essential trace element for all organisms. Many enzymes involved in energy metabolism and reactions with oxygen contain copper as a key component, taking advantage of copper's ability to exist as both +1 and +2 ions to allow the transfer of electrons from one molecule to another.

Although several different compounds are made to react with copper in order to perform the cycle of reactions, it is helpful to first look at the chemical changes occurring to the copper alone. The equations below have been simplified by omitting all of the other species involved in the reactions.

Step 1. Oxidation/reduction	$Cu(s) \rightarrow Cu^{2+}(aq)$
Step 2. Acid-base neutralization and replacement	$Cu^{2+}(aq) \rightarrow Cu(OH)_2(s)$
Step 3. Decomposition	$Cu(OH)_2(s) \rightarrow CuO(s)$
Step 4. Replacement	$CuO(s) \rightarrow Cu^{2+}(aq)$
Step 5. Oxidation/reduction	$Cu^{2+}(aq) \rightarrow Cu(s)$

The following discussion will go into each reaction in more detail. Note that in many cases the equations presented are **net ionic equations**, in which all reacting ions are shown. However, there will often be **spectator ions** that are present and keeping the solution electrically neutral, but not participating in the reaction. In thinking about each step, try to figure out what spectator ions are also present.

Reaction Step 1: Oxidation-reduction reaction

The defining step in an oxidation-reduction (redox) reaction is a shift in electrons from one atom to another. As a formal way of keeping track of the density of electrons around an element we use the **oxidation number**. The oxidation number is a small integer which may be positive, negative, or zero. The loss of electrons around an atom changes its oxidation number to a more positive value, and we say that an atom that has had this change is **oxidized**. An atom that has an increase in electrons has a more negative oxidation number and we say that such an atom has been **reduced**. By convention, the pure form of an element is assigned an oxidation number of 0. In our case, the pure copper metal we start with has atoms with an oxidation number of 0. These atoms lose electron to become Cu^{2+} (aq) ions, with an oxidation number of +2[1]. By definition, copper has become oxidized in this process. The charge lost by copper in this process must be taken up by other atoms in the reaction. Since these other atoms have gained electrons, their oxidation number must become more negative and therefore they are reduced. Any type an oxidation process happens, it must be coupled to a reduction process; charge must be conserved. The full oxidation/reduction reaction is shown below, and the oxidation numbers of all atoms are indicated in the italicized line above the balanced equation.

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[1] For any monoatomic ion, the oxidation number of the element matches the charge of the ion.

Oxidation number

$$\overset{0}{\mathrm{Cu}}\ (s) + \quad 4\ \overset{+1}{\mathrm{H}^+}(aq) + \quad 2\overset{+5\ -2}{\mathrm{NO}_3^-}\ (aq) \rightarrow \overset{+2}{\mathrm{Cu}^{+2}}\ (aq) + \quad 2\ \overset{+4\ -2}{\mathrm{NO}_2}\ (g) + \quad 2\ \overset{+1\ -2}{\mathrm{H}_2\mathrm{O}}\ (l)$$

In this reaction only Cu and N change their oxidation numbers. Note that the change in oxidation numbers must balance so that there is a net charge change of zero. Note that one copper atom has gained 2 units of positive charge, and 2 nitrogen atoms have each lost one unit of positive charge.

The changes in electron amount and location in redox reaction generally change the bond-forming capacity of the reacting atoms. In this case, the reduction of nitrogen in nitrate (a colorless anion) to its reduced form results in the formation of nitrogen dioxide, a nasty orange-brown gas.[2]

Reaction Step 2, first part: Acid-base neutralization reaction

As our starting model, we are calling an acid any substance that releases H^+ ions into aqueous solution. A base releases OH^- ions. In an acid-base reaction, OH^- reacts with H^+ to form water.

The product solution from our first reaction is an acidic solution containing copper(II) ions. We want to react this copper ion with hydroxide ions to form the solid precipitate, $Cu(OH)_2$. There is no chance of doing this until we first remove all of the excess H^+ ions from solution. We will add sufficient base, in the form of an NaOH solution, to neutralize any remaining acid. The addition of still more base will create an excess of OH^-ions which will allow the desired reaction with the copper ions. To help indicate when this stage is reached, we will use an indicator dye (litmus)[3] which has different colors in acidic and basic solutions.

$$H^+(aq) + OH^-\ (aq) \rightarrow H_2O\ (l)$$

Reaction Step 2, second part: A replacement and precipitation reaction

Once a surplus of hydroxide ions has been produced, a replacement reaction occurs. Our best model of $Cu^{+2}(aq)$ is a copper ion surrounded by water molecules. (In the case of copper(II), there are six waters, four held very closely and 2 somewhat more distant.) As the hydroxide ion concentration increases, hydroxide ions can replace these tightly held waters. When 2 hydroxides have replaced waters, neutral $Cu(OH)_2$ is produced. Like most transition metal hydroxides, Cu(II) hydroxide has very poor water solubility and it falls out of solution, forming a precipitate.

$$Cu^{+2}\ (aq) + 2\ OH^-\ (aq) \rightarrow Cu(OH)_2\ (s)$$

Reaction Step 3: A thermal decomposition reaction

When the copper hydroxide is heated, a thermal decomposition reaction occurs. In this case, two stable products can be produced, CuO and H_2O.

$$Cu(OH)_2\ (s) \rightarrow CuO\ (s) + H_2O\ (l)$$

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[2] Nitrogen dioxide is formed as by product of internal combustion engines, resulting from the reaction of atmospheric nitrogen and oxygen at high temperatures. It is an important component in causing photochemical smog, and the removal of this gas from car exhausts is one of the roles of the catalytic converter in the exhaust system.

[3] Litmus is derived from lichens. It is red in acidic solutions, and blue in basic solutions.

The heat provides enough energy to offset the energy in the bonds holding the original hydroxide together and allowing the rearrangement to a new set of bonds to take place. One way to think of this process is that for one of the hydroxide ions, a copper-oxygen bond is broken and a new hydrogen-oxygen bond is formed, using the hydrogen of the other hydroxide ion. This leaves an oxygen with one free bond, which it uses to form another attachment to copper, forming copper (II) oxide.

Reaction Step 4: Another replacement reaction.

After collection of the copper (II) oxide, another replacement reaction takes place. The added sulfuric acid is a strong source of H+ ions. It essentially completely ionizes in water by the following equation:

$$H_2SO_4\ (aq) \rightarrow\ 2\ H^+\ (aq) + SO_4^{-2}\ (aq)$$

We can think of this as a competition in which the high concentration of hydrogen ions in the acidic solution competes with the copper ion for the ability to bind to oxygen. If there are enough hydrogen ions, we can force the system to the point that the oxygen is removed from the copper (essentially O^{-2} + 2 H^+ forming H_2O). This frees the copper(II) ion to go back into solution as the aqueous ion.

$$CuO\ (s) + 2\ H^+ \rightarrow Cu^{+2}\ (aq) + H_2O\ (l)$$

Reaction Step 5: Another oxidation-Reduction reaction.

In the final step we are again doing oxidation-reduction chemistry, as in the first reaction. This time, however, we want to reduce the copper (adding electrons, converting it from Cu^{+2} to Cu^0, the pure metal.) To do this we need a source of electrons. We will use zinc metal as this source. Zinc is easier to oxidize than copper, readily transferring its electrons to the copper ion, in the process forming Zn^{+2} (aq) ions. This is another example of how any reduction reaction must be coupled to an oxidation reaction.

$$Cu^{+2}\ (aq) + Zn\ (s) \rightarrow Cu\ (s) + Zn^{+2}\ (aq)$$

The progress of this reaction can be noted by the disappearance of blue Cu^{+2} (aq) ion as it is replaced by colorless Zn^{+2} (aq).

At the same time, the acidic solution has a large number of H^+ ions. Zinc is also capable of reducing hydrogen ions to form hydrogen gas. You should be able to observe bubbling after the addition of zinc, from the generation of hydrogen gas.

$$Zn\ (s) + 2\ H^+\ (aq) \rightarrow H_2\ (g) + Zn^{+2}\ (aq)$$

When you are completed you should be able to collect copper metal. What properties of your product could help confirm its identity as copper? We will try to provide one additional line of proof. Many elements produce very distinctive colors when heated to high temperatures. (For example, this is often done by geologists as a tool in identifying minerals.) Take a small sample of your product and compare its color reaction in a burner flame with control samples of copper and zinc.

DO NOT do the flame test in the same area where hydrogen gas may be generated. Mixtures of hydrogen and oxygen can burn explosively.

Safety:

1. As usual, always wear appropriate eye protection.

2. Concentrated nitric acid is very damaging to skin and clothes, and its fumes are toxic. All procedures involving nitric acid should be performed in the fume hood. Avoid breathing vapors, and handle with care.
3. The nitrogen dioxide gas generated in step 1 is hazardous. Again, any step generating this gas should be performed in the fume hood.
4. Sodium hydroxide and sulfuric acid are corrosive. Handle with care, and avoid skin and clothing contacts. Spills should be cleaned up promptly.
5. In the final step, flammable hydrogen gas will be generated. We will use no open flames in this laboratory near a reaction that is potentially generating hydrogen gas.
6. Concentrated acids and bases do not go directly down the drain. They should be neutralized first and rinsed down with lots of water. Also, any waste zinc at the end of the lab should not go into the garbage.

Some advice on lab efficiency:

There is a lot to do in this lab, but some habits of work will allow you to leave lab earlier while still obtaining fine results.

1. It is very important that you have read and understood the lab in advance.
2. There will be a lot of beakers moving around the lab. Good labeling avoids lots of extra work!
3. During some time consuming steps, such as boiling or waiting for solids to settle, one or both members of your team can be collecting and assembling materials for later steps. You can note these opportunities in your lab notes or handouts. For example, the clean, dry, tared evaporating dish needed in reaction 5 could be prepared at any earlier time in the procedure. Similarly, dirty glass ware or material used in early steps can be cleaned during pauses in later water.

Procedure:

Reaction step 1:

1a. Weigh a sample of approximately 0.4 g of copper wire or turnings. If turnings are used, wad them into a tight ball to avoid accidental loss.
1b. Place the copper into a clean 250 mL beaker.
1c. In the fume hood, add 3 mL of concentrated nitric acid, slowly and carefully, to the copper. Pour the acid from a 10 mL graduated cylinder. If the copper dissolves readily, go to step 1e.
1d. If the copper does not dissolve readily in step 1c, place the beaker on a hot plate. (Still in the fume hood.) Heat the beaker until the copper is dissolved. Do not boil.
1e. Notice the color of the gas that is evolved. In your notes, there should be observations of any changes that develop during each reaction.
1f. After the copper is dissolved, add 10 mL DI water to dilute the sample for reaction step 2. What is the color of the resulting solution?

Reaction step 2:

2a. Add 6 M NaOH dropwise from a burette or Pasteur pipette while stirring with a glass rod. As you add the NaOH, test the solution for alkalinity by periodically dipping a clean glass stirring rod into the solution and touching a piece of red litmus paper that is lying

on a paper towel. When a drop of your solution turns the litmus blue, the acid has all been neutralized and the solution has turned alkaline. Stop adding NaOH when this result has been reached.
2b. Any observable changes in the solution?
2c. Dilute the solution with DI water to a final volume of about 100 mL in preparation for reaction step 3.

<u>Reaction step 3:</u>
3a. Add a few boiling chips[4] to the beaker and place it on a hot plate.
3b. Boil gently while stirring for about 4 minutes. Record any changes that occur.
3c. Remove the beaker from the heat and set it aside to cool. In another clean 250 mL beaker, begin heating 40 mL of DI water for later use in rinsing your collected solid filtrate.
3d. Prepare a filter paper and funnel for filtration. Use a 250 mL beaker to collect the filtrate.[5] Rinse the clean filter paper and funnel with DI water from a wash bottle, and try to press the filter paper tight against the funnel with your finger to squeeze out air pockets between the paper and the funnel. The system in filtering correctly if the funnel stem fills with water when it is added to the filter cone. Care taken here will greatly speed the filtration process.
3e. Filter the sample, transferring the precipitate to the filter paper. Discard the filtrate, which should be colorless.
3f. Transfer the last traces of solid material from your beaker to the filter, using a stream of DI water from your wash bottle.
3g. Use the DI water you have been heating to wash the solid collected on the filter paper. Pour about 5 mL of the hot water onto the filter paper so that it covers the solid residue and allow it to drain. Repeat this process three or four times.
3h. The filtration apparatus, with your solid residue in place, will move on to reaction step 4. Describe the residue in your laboratory note book.

<u>Reaction step 4:</u>
4a. Dissolve the solid residue of CuO by carefully pouring about 10 mL of 3 M sulfuric acid directly through the residue on the filter into a clean 250 mL beaker. The boiling chips collected should not dissolve. Record any changes that occur. If the solid is not completely dissolved the first time, replace your collection beaker with a new clean one and pour the filtrate from the first attempt back through the filter again. Pour carefully so as to not lose any liquid. Repeat this procedure as often as needed to dissolve all of the CuO solid. It may take four or five times.
4b. When the solid is dissolve, rinse down the wall of the collection beaker that is not under the funnel with cold DI water from a wash bottle and pour this rinse water through the filter into the other beaker. Wash the filter paper and funnel with three or four 5 mL portions of cold DI water and collect these washes into the collection beaker. Your goal here is to get all of the Cu^{+2} ions into one beaker.
4c. Save the acidic solution of copper ions for reaction step 5.

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[4] There are many types of boiling chips, and different materials have different degrees of acid resistance. We will need to use the acid-resistant variety for this laboratory.
[5] Filtrate= liquid that flows through the filter.

Reaction step 5:

5a. Add about 2 g of zinc metal to the copper solution and stir rapidly. Some bubbles of hydrogen gas will be produce during this step. The zinc should be a fresh powder or cut up into very small pieces. Otherwise, this reaction will proceed very slowly, as the rate of the reaction depends on the surface area of the Zn exposed to the solution. The reaction is complete when the blue color of Cu^{+2} (aq) disappears. If any of the blue color remains after all of the zinc has dissolved, add more zinc. (Try about 1 g) until the solution is colorless.

5b. Test for the presence of Cu ions by withdrawing a few drops of solution (with a micropipette or Pasteur pipette) and placing them in a small test tube with 1-2 mL of ammonia (NH_3) solution. Ammonia has a pungent and hazardous vapor, and should only be handled in the fume hoods. A blue color indicates the presence of copper ion.[6] If the presence of Cu ion was indicated, rinse the test tube and pipette with DI water back into your original acid –zinc solution and retest after the added zinc has reacted. If there is excess zinc after all of the copper has reacted, add 3 M HCl to dissolve the excess zinc.

5c. Allow the copper metal precipitate to settle. Decant the supernatant liquid carefully, and avoid the loss of any solid. Do not decant directly into the sink; instead, decant into a clean beaker. This will allow the recovery of any metal that is lost during the decanting step. You will still have some liquid left with your product metal.

5d. Wash your copper metal precipitate by decantation at least three times. To wash, add clean DI water to your copper metal, mix well and allow the solid to settle. Pour off the wash water, and then repeat. Again, it is best to decant into a waste beaker as insurance against losing your product.

5e. Record the mass of a clean dry evaporating dish.

5f. Transfer all of the washed copper precipitate from the beaker to the evaporating dish. Use a rubber policeman or a small spatula to sweep out all of the solid and flush any small bits out with DI water from a wash bottle. Be sure to rinse your spatula onto the evaporating dish.

5g. Let the solid settle in the evaporating dish and carefully decant off most of the water.

5h. Place the evaporating dish into the drying oven. (You should record the temperature of the oven.) Place the dish into the oven on a small paper towel with your names and lab section. After the dish and its contents are dry, remove it from the oven and allow it to cool to room temperature.

5i. Weight the dish and its contents and record the mass. Your results should include the mass of copper recovered and the percent copper recovered.

Per cent copper recovered = mass of product copper/mass of starting copper x 100 %

If there is time, also try to confirm the identity of your product as copper by a flame test.

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[6] This test takes advantage of the color produced by the $Cu^{+2}(NH_3)_2$ ion, which is even more brightly colored than the ion in water alone.