Name:

Chemistry 118 Laboratory University of Massachusetts Boston

COPPER TRANSFORMATIONS

LEARNING GOALS

In this laboratory exercise you will start with solid copper and chemically transform it soluble copper ions and then back to solid copper again. It was designed with the following learning goals in mind.

- 1. Practice in doing stoichiometry problems
- 2. Instill a deeper understanding of the concepts of conservation of mass
- 3. Become familiar with different classes of reactions
- 4. Begin to appreciate the relationship between the interactions of the outermost electrons and macroscopic properties

INTRODUCTION

In this experiment we will carry out several reactions of the element copper (symbol Cu). These are summarized as a Schematic Diagram at the end of the manual. Essentially, you will take copper metal on a journey of chemical transformations, only to end up with solid copper metal once again. In the process we will learn new laboratory techniques, practice mole calculations involving chemical equations and gain experience with many of the types of reactions studies in this course, such as precipitation reactions, acid-base reaction and redox-reactions and we will be able to calculate the extent the copper metal present in the beginning of the experiment was recovered.

<u>EXPERIMENT</u>

Reaction of Metallic Copper with Nitric Acid Solution

- 1. Obtain a piece of copper wire and measure its mass on an analytical balance. Record the mass on the proper line on the top of page 8.
- 2. Roll the wire into a flat coil and place it in a clean 150-mL beaker labeled with your initials.
- 3. Use a 10 mL graduated cylinder to measure 3 mL of deionized water into the beaker.
- 4. In the fume hood dispense 3.0 mL of HNO₃ solution into the beaker. Move to a fume hood

with a hot plate. Warm the beaker to get the reaction started and then leave it in the hood.

WARNING! NITRIC ACID IS CORROSIVE. IF ANY ACID CONTACTS YOUR SKIN OR SPILLS ANYWHERE, WASH IT UP IMMEDIATELY.

The reaction going on in the beaker is described by the following balanced equation:

(1)
$$3Cu_{(s)} + 8HNO_{3(aq)} \rightarrow 3Cu(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O$$

The brown gas is NO₂ (nitrogen dioxide), which is formed by reaction of NO_(g) (nitric oxide) with O_{2(g)} (oxygen gas) in the air. These nitrogen oxide gases are toxic. *Keep the beaker in the fume hood until the gas evolution stops.* Notice that the solution is blue. The aqueous Cu(NO₃)₂ (copper nitrate) is dissociated into Cu²⁺ (copper) ions and NO₃⁻ (nitrate) ions and the Cu²⁺ ions are blue due to a phenomenon known as d-orbital splitting. Water molecules interact with the Cu²⁺ ions in such a way that an energy gap develops between electrons located in d-orbitals (represented by the middle block of the periodic table). Electronic transitions between these two levels match the energy of orange light. Therefore, when light strikes the solution, only the blue light is reflected back to our eyes because the orange light is absorbed (see the color wheel below).



This reaction is an example of a type of reaction called a red-ox (reduction/oxidation) reaction. In a red-ox reaction one reactant is oxidized by losing one or more outer electrons and one is reduced by gaining these electrons. In this example copper is being oxidized to form Cu^{2+} and the N in HNO₃ is being reduced (from an oxidation state of +5) to form the nitrogen in NO_(g) (oxidation state of +2). Since HNO₃ and Cu(NO₃)₂ are completely dissociated in water to produce H⁺ and NO₃⁻ and Cu²⁺ and NO₃⁻, the reaction can be more succinctly written as its net ionic equation.

(2)
$$3Cu_{(s)} + 8H^{+}_{(aq)} + 2NO_{3(aq)} \rightarrow 3Cu^{2+}_{(aq)} + 2NO_{(g)} + 4H_2O$$

If it often useful to break a redox reaction down into its half reactions. In this example

Reduction $8H^{+}_{(aq)} + 2NO_{3}_{(aq)} + 6e \rightarrow 2NO_{(g)} + 4H_2O$ Oxidation $3Cu_{(s)} \rightarrow 3Cu^{2+}_{(aq)} + 6e$ -

Wait until the copper wire disappears. What does the disappearance of the copper wire mean? Consider the following possibilities:

- a. Copper was the limiting reagent and HNO₃ was in excess.
- b. HNO₃ was the limiting reagent and Cu was in excess.
- c. Neither Cu nor HNO₃ was added in excess.

Which of these is possible?	a.	b.	c.
Which is impossible?	a.	b.	c.

Explain your answers.

5. Add about 25 mL of deionized water measured by graduated cylinder to the beaker and bring it back to your bench.

Precipitation of Copper Hydroxide

- 6. Gather up the following:
 - a glass stirring rod
 - a 10-mL graduate cylinder
 - two strips of red litmus paper
 - a 50-ml beaker
 - a medicine dropper
 - a wash bottle filled with deionized water
- 7. Measure out about 6 mL of NaOH (sodium hydroxide) solution using the 10-mL graduated cylinder. Transfer this to the 50-mL beaker.

- 8. Dip the stirring rod into the copper nitrate/nitric acid solution and then touch it to the red litmus paper. Notice the color remains red which indicates that the solution is acidic.
- 9. Rinse off the stirring rod, dip it into the NaOH and then touch the litmus paper. Notice the color turns blue which indicates that the sodium hydroxide solution is alkaline.
- 10. Slowly add NaOH solution dropwise and with continuous stirring just until the solution turns alkaline. Notice that a blue precipitate forms, but redissolves at first when the solution is still very acidic. Eventually when enough NaOH is added, the precipitate remains. STOP ADDING NaOH WHEN THE SOLUTION IS ALKALINE as indicated by a blue litmus test.

There are two reactions going on when NaOH is added. Reaction 3 describes the precipitation of the blue solid $Cu(OH)_2$ (copper hydroxide).

(3)
$$Cu(NO_3)_{2(aq)} + 2 NaOH_{(aq)} \rightarrow Cu(OH)_{2(s)} + 2 NaNO_{3(aq)}$$

NIE $Cu^{2+}_{(aq)} + 2OH_{(aq)}^{-} \rightarrow Cu(OH)_{2(s)}$

and Reaction 4 describes the neutralization of the excess nitric acid by the base NaOH.

(4)
$$HNO_{3(aq)} + NaOH_{(aq)} \rightarrow NaNO_{3(aq)} + H_2O$$

Reaction 3 is an example of a type of reaction called a precipitation reaction. A precipitation reaction occurs when a solution containing a specific cation is mixed with a solution containing a certain anion at concentrations that are above a threshold $([Cu^{2+}][OH-]^2 > Ksp(Cu(OH)_2))$. The two ions combine together to form an insoluble salt. In this example Cu^{2+} is the cation, OH^- is the anion, $Cu(OH)_{2(s)}$ is the precipitate and $Ksp(Cu(OH)_2)$ is the solubility product constant of copper (II) hydroxide.

Reaction 4 is an example of a type of reaction called an acid-base reaction. In an acid-base reaction the acid donates a proton to a base. In this example $HNO_{3(aq)}$ is a strong acid and $NaOH_{(aq)}$ is a strong base.

- 11. Add another 25 mL of deionized water to the beaker containing the precipitate.
- 12. Set up a suction filtration apparatus with a piece of wet filter paper in the funnel. Your instructor will demonstrate how to use this apparatus.
- 13. Filter the solid from the solution. Use a stream of water from the wash bottle to transfer all the solid Cu(OH)₂ from the beaker. Continue the suction until the cake of solid on the filter paper looks dry.

14. Clean up

- Discard the litmus papers.
- Rinse out the graduated cylinder, both beakers and the dropper.
- Wash off the stirring rod.
- Discard the liquid in the filter flask. Rinse out the flask.

Dissolving Solid Cu(OH)₂ by Reaction with Hydrochloric Acid

- 15. Gather up clean glassware:
 - a 250 mL beaker.
 - a medicine dropper.
 - a 50 mL beaker.
- 16. Label the 250-mL beaker with your initials. Set the filtration funnel with the cake of solid Cu(OH)₂ into the beaker.
- 17. Dispense 10 mL of HCl (hydrochloric acid) solution into the 50-mL beaker. Use the dropper to place drops of HCl solution directly on to the blue solid.

Notice that the solid gradually dissolves and the liquid runs through the filter paper into the beaker. Notice also that HCl solution first turns yellow and then appears blue-green in the beaker.

18. Continue dropping HCl solution into the funnel until all the solid is dissolved. If the filter paper has any color at all, add drops of deionized water until all colored solution is washed through.

When the HCl solution first contacts solid $Cu(OH)_2$, the H⁺ (hydrogen ions) and the Cl⁻ (chloride ions) in the HCl react with $Cu(OH)_{2(s)}$ according to

(5) $\operatorname{Cu}(\operatorname{OH})_{2(s)} + 2\operatorname{H}^{+}_{(aq)} + 3\operatorname{Cl}^{-}_{(aq)} \rightarrow \operatorname{Cu}\operatorname{Cl}^{-}_{3(aq)} + 2\operatorname{H}_{2}\operatorname{O}$

The yellow color is caused by the complex ion $CuCl_3$. This is the also the result of d-orbital splitting, but the energy gap is smaller because Cl^- is a weaker ligand than water. The electronic transitions between these two levels match the energy of purple light. Therefore, when light strikes the solution, only the yellow light is reflected back to our eyes because the purple light is absorbed (see color wheel above).

As the solution becomes diluted, the $CuCl_3^-$ ions tend to lose Cl^- and their color shifts towards green (indicating a mixture of different copper/chloride species) and eventually to blue

(indicating Cu²⁺ions). When the solution is blue, the overall change is

(6)
$$\operatorname{Cu}(\operatorname{OH})_{2(s)} + 2\operatorname{HCl}_{(aq)} \rightarrow \operatorname{CuCl}_{2(aq)} + 2\operatorname{H}_2\operatorname{O}$$

These reactions (5 and 6) can be classified as both an acid-base reaction and dissolution reaction. In dissolution reaction of solid salt dissolves in solution.

19. Discard the filter paper and rinse out the filter funnel.

Conversion of Copper Ion to Copper Metal

- 20. Use a triple-beam balance to weigh out about 1 gram of Zn (zinc) metal onto a weighing dish.
- 21. Bring this weighing dish and your 250 mL beaker containing the copper solution to a fume hood and add the zinc to the beaker.

Notice the change in appearance of the metal and the evolution of gas. There are two reactions occurring here. One is the reaction of copper ion in $CuCl_2$ with metallic zinc according to

(7)
$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

The change in appearance of the solid is the coating of copper metal on the zinc. Notice that as the reaction proceeds the blue color of the solution gradually disappears as the colorless Zn^{2+} (ions) replace the blue Cu^{2+} ions in the solution. This is a redox reaction. The Zn metal is giving up two electrons to the Cu^{2+} ions. The Zn(s) is being oxidized and the Cu^{2+} is being reduced.

Reduction	$Cu^{2+} + 2e \rightarrow Cu_{(s)}$
Oxidation	$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e$

The second reaction is the reaction of the excess hydrogen ions in the hydrochloric acid with zinc metal according to

(8)
$$Zn(s) + 2HCl(aq) \rightarrow H_{2(g)} + ZnCl_2(aq)$$

The gas bubbles are H_2 (hydrogen gas). This is also a redox reaction. Each Zn metal atom gives up two electrons, one to each H^+ to form H_2 . The Zn(s) is being oxidized and the H^+ is being reduced.

Reduction	$2\mathrm{H}^+$	+	2e- \rightarrow	$H_{2(g)}$
Oxidation	Zn _(s)	\rightarrow	$Zn^{2+}_{(aq)}$	+ 2e-

- 22. As the evolution of gas slows down, use a glass stirring rod to agitate the mixture breaking up clumps of copper metal that tend to coat the remaining zinc metal. Continue occasional stirring until the gas bubbles stop.
- 23. Add about 5 mL of HCl solution from the 50-mL beaker. If gas bubbles form again, continue stirring and occasionally adding a few mL of HCl until no more gas bubbles form. This will take some time. In the meantime work on the problems starting on page 6.
- 24. Wash the copper metal two or three times by adding deionized water (roughly to the 50 mL line on the beaker), stirring, allowing the metal to settle and decanting (carefully pouring off) the wash water.
- 25. Pour off as much liquid as possible and set your beaker on a warm (not hot) hotplate to dry it out.

Examine the dry metal powder in the beaker. This is the same copper that was in your original wire. If you did not lose any along the way and if the copper powder is pure, the mass of this powder would be the same as your wire.

- 26. Discard the powder into the WASTE COPPER beaker and return all equipment to the proper places.
- 27. Clean up.

Name	Lab Section
Partner(s)	

<u>Reactions of Copper</u> Data

Mass of your copper wire _____g (4 decimal places)

PROBLEM 1. Considering that the atomic mass of Cu is 63.54 g/mol, calculate the moles of copper and the millimoles of copper in your wire.	moles of Cu:	mmol Cu
PROBLEM 2. The nitric acid has a concentration of 16 moles per liter (or 16 millimoles per mL). If you added 3.0 mL of this acid to your beaker, calculate the moles and millimoles HNO ₃ in this 3.0 mL.	mol HNO3	mmol HNO3
PROBLEM 3. This problem refers to Reaction 1. The observed disappearance of the copper wire might indicate that	 a. How much HNO₃ (in millimoles) reacted with your wire? b. Compare this with your answer to PROBLEM 2. The limiting reagent 	mmol HNO₃
Cu was the limiting reagent. We now check this by a calculation.	1S:c. How much HNO₃ (in millimoles) remains unreacted with Cu(s)?	:mmol HNO₃
	d. How much Cu(NO ₃) ₂ is produced?	mmol Cu(NO ₃) ₂
PROBLEM 4. Suppose you add just enough NaOH so that all the $Cu(NO_3)_2$ is converted to solid $Cu(OH)_2$ by Reaction 3 and all the remaining HNO ₃ is neutralized in Reaction 4.	a. How much NaOH is needed in Reaction 3?	mmol NaOH
	b. How much NaOH is needed in Reaction 4?	mmol NaOH
	c. The total NaOH needed is:	mmol NaOH
	d. How much Cu(OH) ₂ is produced?	mmol Cu(OH) ₂
PROBLEM 5. The NaOH solution contains 10.0 moles per liter or 10.0 mmol/mL.	a. What volume is needed to provide the total quantity calculated in Problem 4c?	mL NaOH

	b. Suppose that the average size of your drop was 0.050 mL. How many drops would be needed to supply the total NaOH requirement?		Drops
PROBLEM 6. Refer to Reaction 5.	a. How much HCl is needed to dissolve all the solid Cu(OH) ₂ ?	mmol HCI	
	b. The HCl solution concentration is 6.0 moles per liter (or 6.0 mmol per mL). What volume is required?		mL HCI
	c. How much CuCl ₂ is produced?		mmol CuCl ₂
PROBLEM 7. Suppose that you weighed out 1.1 grams of zinc metal (65.4 g/mol). Calculate the moles and millimoles of this metal.	mol Zn		mmol Zn
PROBLEM 8. Refer to Reaction 7.	a. Assuming that the zinc is in excess, how much copper metal is produced?	mol Cu	mmol Cu
	b. What mass of Cu metal is produced?		g Cu
	c. How much zinc remains after Reaction 6 is completed?	mol Zn	mmol Zn
PROBLEM 9. Refer to Reaction 8.	a. How much HCl reacts with all the remaining metallic zinc calculated in Problem 8c?	mol HCl	mmol HCI
	b. The HCl solution contains 6.0 mol/L (or 6.0 mmol/mL). What volume is needed?		mL HCl



10

Lab Report

No abstract required

Submit the data sheet (pg 8 and 9) and a discussion of your results. It is worth 30 pts.

In a paragraph report the percent recovery of the copper (15 pts) and explain your results (15 pts). If your result is over 100 %, what does this mean and how do you account for it? If your result is under 100 %, what does this mean and how do you account for it?