Does Copper Metal React with Acetic Acid?

Stephen DeMeo
Department of Chemistry, Hunter College of the City University of New York, New York, NY 10021

I often measure the success of a laboratory activity on how well my students are able to think like scientists: that is, to think analytically and solve problems. One laboratory activity that shows promise in promoting this kind of thinking begins after my class has studied redox reactions and some acid–base theory. I initiate the activity by simply asking my introductory chemistry students to determine if copper metal reacts with acetic acid. While the answer to this question is known (*1*), solving this problem does give students experience with important scientific processes that are generalizable to new laboratory experiences. For example, in the course of this investigation students hypothesize answers, control variables by designing an experiment, and make logical deductions based on what they know and observe. The following discussion will elaborate on the methods my students have used to solve this problem.

The Discrepant Event

When faced with the question, "Does copper metal react with acetic acid?" the initial response of most students is either to refer to their textbooks or to conduct an experiment. The general chemistry textbooks that I have surveyed do not answer this question explicitly. While most state that copper reacts with concentrated nitric and sulfuric acids, copper is usually described as unable to displace hydrogen from acidic solutions or unreactive with nonoxidizing acids (*2–4*). While it might be inferred from this that copper does not react with acetic acid, other publications such as *The Merck Index* states that "copper is attacked by acetic acid" (*5*). The inability to find a conclusive and well described answer from these sources stimulates students to conduct an empirical investigation.

Designing an Experiment

Most students initially design a very simple experiment such as "add acetic acid to copper and see what happens." Although this initial exploration is fine, I ask them to consider all chemical and physical variables, even the gases in the air, and how they might control for each variable. The following generic procedure and design give very good results.

Into four screw-top test tubes, add 3 mL of a 50/50 solution of glacial acetic acid and distilled water.[1] Next, cut four pieces of copper wire each 4 cm in length, scrape them clean with fine sand paper, remove any particulate matter with a paper towel, and then place each wire into a test tube containing an acid solution. In order for all of the copper to come into contact with the solution, the copper wire can be bent in half or cut into two equal pieces. To investigate different atmospheric variables, the four test tubes should be prepared as described below, sealed with a screw-cap, wrapped in Parafilm, and observed over time. A fifth test tube can act as a control.

#1. Cu + 50% acid/50% water + air
#2. Cu + 50% acid/50% water + mostly oxygen
#3. Cu + 50% acid/50% water + mostly carbon dioxide
#4. Cu + 50% acid/50% water + mostly nitrogen
#5. Cu + water + air

Test tubes #2–4 are designed to determine if specific components in the air are causes of a reaction. Oxygen can be prepared by adding 30 mL of 3% hydrogen peroxide to 0.25–0.50 g of manganese dioxide in a 125-mL sidearm flask. Oxygen can be bubbled through the acid solution by stoppering the flask and attaching one end of a rubber hose to the side arm and the other end to a Pasteur pipet. Carbon dioxide can be prepared by adding vinegar (5% acetic acid in water) to sodium bicarbonate (baking soda), and can be dispensed in a similar manner. Nitrogen can be purchased commercially or can be made by adding dilute nitric acid to sulfamic acid crystals.

Observations

A representative data table can be seen below. Except for weekends when students could not be present in class, observations were recorded daily over a two week period (see Table 1).

Interpretations and Additional Tests

Based on the above data, two important interpretations can be made by most introductory chemistry students:

- The changes in color of the copper wire and the solution in test tubes #1 and #2 indicate that a reaction or reactions occurred. The absence of changes in the other test tubes suggest that no reactions occurred.
- The changes in test tubes #1 and #2 and the absence of changes in the other test tubes suggest that oxygen played a role in the reaction or reactions found in test tubes #1 and #2.

The first claim can be strengthened by conducting a quick qualitative test for copper(II) ion in all of the test tubes. Test tubes #1 and #2 gave a positive test for copper(II) ion, while the others were negative.[2] The second interpretation can be supported further by preparing a sixth test tube with a 50/50 solution of glacial acetic acid and *boiled* water, copper wire, and a 1–2 cm layer of paraffin oil. The boiled water and paraffin oil (which prevents oxygen in the air from dissolving into the acid solution) were used to determine if copper would react with acetic acid in a medium that contained very little oxygen. Experimentally, it was found that even after 15 days, the solution in test tube #6 did not turn blue. This result supported the final contention that copper metal reacts with acetic acid in the presence of oxygen within the time frame studied.

A review of the literature indicates that oxygen does play an important role in the reaction between copper and acetic acid. The mechanism that has been proposed involves the formation of a free radical and an electrochemical corrosion process (*1*). While mechanistic details are not appropriate for introductory students, suffice it to say that the mechanism does involve formation of a strong oxidizer, peroxoacetic acid (CH_3COOOH), from dissolved oxygen, as well as the production of a copper oxide and a copper ion. It is highly likely that a copper oxide is responsible for the tarnish on the surface of the copper metal, while the production of copper(II) ion accounts for the blue color change in test tubes #1 and #2.

It was evident from observations of test tubes #3, #4, and especially #6 that no reactions between copper metal and acetic acid occurred in the absence of oxygen. This is in keeping with electrochemical theory. Since copper is below hydrogen in the electrochemical series, copper is reluctant to displace hydrogen ions from electrolytes. In terms of standard electrode potential, copper has a potential of −0.34 volts ($Cu \rightarrow Cu^{2+} + 2e^-$), while hydrogen has a greater potential of 0.00 volts ($2H^+ + 2e^- \rightarrow H_2$). The emf of the cell would be negative and therefore the reaction would be nonspontaneous under standard conditions. When oxygen is involved in the reaction between copper and acetic acid, the electrochemical series and the standard electrode potentials cannot be used as a guide to determine if the reaction is spontaneous. A generalized relationship between copper metal and acids is nicely described by Massey: "Although copper metal will dissolve readily in an oxidizing acid such as nitric acid it will not dissolve in a nonoxidizing acid unless either an oxidizing agent or a suitable complexing agent is present also" (*6*). With respect to this experiment, it is assumed from the literature that the formation of the strong oxidizing agent, peroxoacetic acid, oxidizes copper metal to a copper oxide (*1*).

Table 1. Student Observations of Test Tubes over Time

Day	Test Tube Number[a]				
	1	2	3	4	5
1	nc	nc	nc	nc	nc
2	some tarnish	nc	nc	nc	nc
3	some tarnish	some tarnish	nc	nc	nc
4	meniscus is tinted light aqua-blue	meniscus is tinted light aqua-blue	nc	nc	nc
5	meniscus is tinted light aqua-blue	meniscus is tinted light aqua-blue	nc	nc	nc
8	tarnish darkens; solution is light blue throughout	tarnish is not as dark as test tube #1; solution is tinted light aqua-blue	nc	nc	nc
9	solution is light blue throughout	solution is light blue throughout	nc	nc	nc
10	solution becomes bluer	solution becomes bluer	nc	nc	nc
11	tarnish is still present; solution remains aqua-blue	tarnish is still present; solution remains aqua-blue	nc	nc	nc
12	tarnish is still present; solution remains aqua-blue	tarnish is still present; solution remains aqua-blue	nc	nc	nc
15	tarnish is still present; solution remains aqua-blue	tarnish is still present; solution remains aqua-blue	nc	nc	nc

[a]nc = no change.

Conclusion

Without relying on sensitive instrumentation, students were able to conclude that oxygen plays an important role in the interaction of copper metal with acetic acid. This led them to realize that the conditions under which two reactants interact are important in determining the type of products that are made. When the *Merck Index* says that "copper is attacked by acetic acid", it is assumed that the phenomenon is occurring in air. On a physical level, this is similar to saying that water boils at 100 °C—it is assumed that the pressure is 1 atmosphere.

This activity could be used to discuss the electrochemical series, redox, or the solubility of gases in water, as well as to introduce the concept of corrosion. Further investigations might include varying the concentration of acetic acid or spectrometrically determining the amount of copper ion produced over time. It might also be interesting to determine the effect of other oxidizing agents such as hydrogen peroxide on copper and acetic acid, or to investigate interactions between copper metal and other nonoxidizing acids such as HCl.

Because of the simplicity of the experimental design, this activity would be appropriate for introductory chemistry students and could function as a discovery-oriented laboratory activity or as an individualized project. While the necessity of recording data every day would not fit the schedule of many large colleges, other settings such as high schools and small residential colleges could accommodate this requirement without much difficulty.

This activity was initiated from a discrepant event, an event which will propel the student to design an experiment, collect and interpret data, and finally come to an awareness that the question originally asked must be reformulated to a more accurate portrayal of their investigation. By asking instead, "Will copper react with acetic acid in the presence of oxygen?" students will work like scientists actively altering their line of inquiry as they move between methodology and theory.

Acknowledgments

I am gratefully indebted to the reviewer of this manuscript and the Barnard College faculty. Special thanks goes to Jim Carter for his experimental insights during the workup of this activity, and to Leslie Lessinger for his editorial comments.

Notes

1. Three milliliters is used in order to observe the solution turn blue within a few days. With a greater volume a color change cannot be ascertained until days later. (**Caution**: if not used properly, glacial acetic acid can cause damage to the skin. It is recommended that instructor prepare the acid solution before class; it should be dispensed from eye dropper bottles to minimize spills. If contact is made with acetic acid, immediately wash the area with soap and water followed by a solution of baking soda.)

2. Solutions containing copper(II) ion are usually blue and give a green flame test. Addition of excess solid zinc metal transforms the solution under test from blue to colorless. Addition of sulfide ion will lead to a black precipitate of copper(II) sulfide in acidic solutions.

Literature Cited

1. Anuchin, P. I. *Sb. Tr., Tsent. Nauch.-Issled. Proekt. Inst. Lesokhim. Prom.* **1971,** *21*, 124–130
2. Ebbing, D. D. *General Chemistry*, 4th ed.; Houghton Mifflin: Bos-

ton, 1993.
3. Zumdahl, S. S. *Chemistry*, 3rd ed.; D. C. Heath: Lexington, MA, 1993.
4. McQuarrie, D. A.; *General Chemistry*, 3rd ed.; W. H. Freeman: New York, 1991.
5. *The Merck Index*, 11th ed.; Budavari, S., Ed.; Merck: Rahway, NJ, 1989; p 393.
6. Massey, A. G. In *Comprehensive Inorganic Chemistry*; Trotman-Dickenson, A. F., Ed.; Pergamon: London, 1973; Vol. 3, p 18.