Electrochemical Production of Hydrogen Gas and Copper(II) ion
Iodometric Titration of Copper(II) ion

Electrolysis of water solutions in which one electrode is made of a material more easily oxidized than water results in the dissolution of that electrode. This process is used industrially to purify metals, particularly copper. In that case, the copper which is oxidized is in the form of an impure anode. The resulting copper(II) ions then plate onto a pure Cu cathode, leaving impurities behind.

In this experiment, the copper oxidized remains in the solution and the presence of acid allows H^+ ion to be reduced at the relatively inert stainless steel cathode to form H_2 gas. Thus *in this electrolytic cell, an external voltage causes copper metal to be oxidized to copper(II) ion and H^+ ion to be reduced to hydrogen gas.*

The amount of copper electrolyzed can be determined in a variety of ways. The electrode can be massed before and after. The electrical work involved can be used to determine the amount of Cu using Faraday's laws. The concentration of Cu^{2+} in solution can be determined with a colorimeter. Or the Cu(II) can be titrated with a suitable reducing agent. All of these methods are employed in this experiment:

(1) The mass change of the copper electrode is too small to permit precise determination on the centigram balances, but it can be used as a ballpark check on the overall results.

(2) The Faraday determination is similar to that done in the plating of zinc metal.

(3) The copper(II) ion from the oxidation of the electrode colors the solution blue and could be determined directly by a sensitive colorimeter, but the concentration is too small for our equipment. This is not an uncommon problem and there is a common solution: add something to the mixture which intensifies the color (or creates a new one). Aqueous ammonia reacts with copper(II) ion to form a deep blue complex ion, $Cu(NH_3)_4^{2+}$. A calibration curve for this ion in solution is provided with this handout.

(4) To allow for comparison of the techniques and to illustrate the process of **redox titration** (in this case, *iodometric titration*), the copper(II) ion in solution will also be titrated as described on the facing page.

(5) Finally, the volume of hydrogen gas collected may also be used to confirm the copper calculations from Faraday's laws, using the ideal gas law.

Adapted from: <u>Electrochemical Production of Hydrogen Gas and Cupric Ion. The Iodometric Titration of Copper</u>, J. McCullough and H. Stone, *Experimental General Chemistry*, McGraw Hill, 1953

Iodometric titration of transition metals is often accomplished using thiosulfate ion ($S_2O_3^{2-}$) as a reducing agent. In this case iodide ion (from solid KI) is used to reduce the copper(II) produced by the electrolysis to copper(I) which is insoluble with iodide. The iodide ion is oxidized to I_2 which reacts with excess iodide in the solution to form the brown triiodide ion (I_3^-)

$$2\ Cu^{2+}(aq) + 5\ I^-(aq) \rightarrow 2\ CuI(s) + I_3^-(aq) \qquad (1)$$
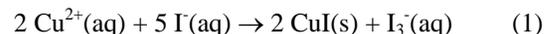
[the triiodide ion is considered equivalent to $I^- + I_2$]

Titration of the triiodide ion (I_3^-) is then begun by adding $Na_2S_2O_3$ solution:

$$I_3^-(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 3\ I^-(aq) + S_4O_6^{2-}(aq) \qquad (2)$$
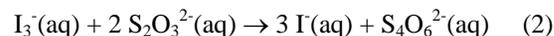
The brown color gradually fades to a light beige color as the titration proceeds. At this point, starch indicator is added, which causes the solution to turn blue-grey (I_2 + starch $\rightarrow$ blue-grey complex). Continued addition of thiosulfate ion results in the disappearance of the blue color as I_3^- is reduced to I^-. The final solution is white. Once the solid KI has been added to the solution the titration should be completed quickly (but not recklessly!!) for best results since copper(I) ion is readily oxidized in the air and this will tend to produce inaccurate results.

Preparing to experiment

You will be supplied with the following materials:

1. 6 M H_2SO_4 (use about 3 mL)
2. a copper electrode and a stainless steel electrode
3. a current probe
4. a colorimeter w/cuvette
5. a power supply (set on 12 volts)
6. 0.050 M $Na_2S_2O_3$ solution
7. solid KI (use about 2.5 g)
8. 6 M NH_3(aq)
9. starch solution (use about 3 mL)
10. a buret and clamp
11. magnetic stirrer/stirring bar
12. two 1 mL calibrated beral pipets
13. a 100 mL graduated cylinder

Design an experiment to electrolyze an acidic solution using a copper anode and a stainless steel cathode, collecting the hydrogen gas (about 25 mL). Determine $[Cu^{2+}]$ in the resulting solution by redox titration as described in the introduction, by the volume of H_2 collected, the mass change of the copper electrode, and the absorbance of a sample of the copper(II) solution reacted with aqueous ammonia.

BE SURE TO BRING YOUR TI-83/84 CALCULATOR TO CLASS FOR THIS EXPERIMENT. YOU WILL ALSO NEED A COPY OF THE HCHEM.83G FILES IN YOUR CALCULATOR MEMORY.

Pre-lab take-home quiz

These questions should be answered on a separate sheet of paper to be turned in on the day you do this experiment.

1. Write the balanced equation for the reaction that occurs during the electrolysis.

2. Add reactions (1) and (2) on page 1 to obtain the overall reaction of $S_2O_3^{2-}$ with Cu^{2+} during the titration.

3. During a titration as described in the introduction, 15.5 mL of 0.15 M $Na_2S_2O_3$ is used to reach the endpoint of a copper solution. How many moles of copper are present?

4. In order for the copper electrode to dissolve during the electrolysis, which terminal of the power supply should it be connected to (+ or -)?
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Technique

1. An electrolysis set-up:
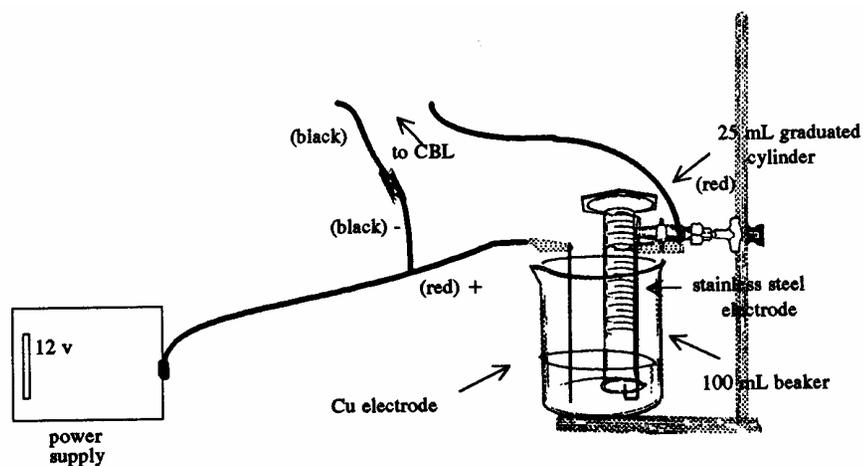
Notice that the electrode attached to the (+) terminal of the power supply is made of copper. If you follow the circuit through the interface you will also see that the negative (-) lead from the power supply is indirectly attached to the stainless steel electrode under the gas measuring tube. Since electrons are supplied at this electrode, this is where water will be *reduced* to hydrogen gas. Also, a little of the metal portion of the electrode must be exposed outside the graduated cylinder or else the electrolysis will be slow. In order to minimize the amount of water used for the electrolysis, begin by filling the 25 mL graduated cylinder and 100 mL beaker in a bucket of water (your instructor will demonstrate). Once the apparatus is clamped in place [you can use the clamp to help hold the stainless steel electrode in the proper position, centered in the cylinder mouth with a little metal exposed below the cylinder], use a turkey baster to remove as much water as possible (you should have no more than about 60 mL in the beaker). Then add the 3 mL of acid.

2. Measuring current again

You can use the same technique to measure current in this experiment as you used in plating. Hook up the entire circuit but leave the copper electrode out of the solution. When you are ready to begin, wait until time zero appears on your calculator screen and then insert the copper electrode into the solution. Recording every 15 seconds will be sufficient. Watch the gas collection carefully. You don't want to exceed the 25 mL mark so be sure to pull the copper electrode out at the nearest time reading that will give close to 25 mL of gas.

3. Determining the gas volume in the graduated cylinder

If you want to figure out how much hydrogen you have in the gas measuring tube, the volume will not be enough information. You will also need the temperature and pressure. You may remember a trick we used earlier in the year to make the pressure in a gas measuring tube equal to the room pressure. Be sure the liquid level inside the cylinder is the same as the liquid level in the beaker before recording the volume of gas. The room temperature and pressure will be posted.

4. The solution

Once the electrolysis is complete, and the volume of gas has been measured, you need to drain the remaining liquid in the cylinder into the beaker (hence the limitation on total volume of water). The beaker of solution should then be transferred into a 100 mL cylinder and small rinsings of the beaker used to bring the total volume to 100.0 mL. Then pour the resulting solution into a clean 250 mL beaker and mix well. All of your copper(II) is now in this beaker. 1.5 mL of this solution is removed by pipet and added to 1.5 mL of 6 M NH_3 in a cuvette to make the solution for the colorimeter (the blank is water). The remaining 98.5 mL is used for the titration.

5. The titration

        Once the solid KI is added, the solution turns brown and $Na_2S_2O_3$ is added from the buret until the color becomes beige (BUT NOT WHITE). Then add 3 mL starch and titrate to white.

6. Finally, use the calibration curve below to determine the moles of copper(II) ion in your mixture [the calibration curve was produced by treating 1.5 mL of standard copper(II) solutions in the same way you treated yours, so you can get the $[Cu^{2+}]$ in the 100 mL of original solution directly from the graph--you still need to calculate moles]. Is there good agreement with the result in #2?

Analysis

1. Determine the approximate number of moles of copper oxidized from the mass change of the electrode.

2. Use your data to determine the moles of hydrogen gas collected during the electrolysis. Because the graduated cylinder was intended to be read upright, there is a consistent error in reading the volume upside down. Repeated measurements show that the error is about +4%. For a 25 mL cylinder, this means that the volume you record looks 1 mL larger than it really is. Also, don't forget to correct for the water vapor pressure (table below).

Calibration curve for Cu(NH$_3$)$_4$$^{2+}$ at 635 nm

y = 28.07x - 0.0046

Vapor Pressure of Water

Temperature, °C	Pressure, mm Hg	Pressure, kPa
19	16.5	2.20
20	17.5	2.33
21	18.7	2.49
22	19.8	2.64
23	21.1	2.81
24	22.4	2.99
25	23.8	3.17
26	25.2	3.36

3. Compare the approximate moles of copper with the moles of hydrogen. Based on the balanced electrolysis equation, do these values roughly agree?

4. Use your time and current data to determine the moles of Cu that dissolved. Compare this to #2. Is there good agreement?

5. Based on the ratio of $S_2O_3^{2-}$ to Cu^{2+} in the titration balanced equation and the volume of thiosulfate used in the titration, determine the moles of copper present in the 100 mL of solution. Remember, you only titrated 98.5 mL of the original solution [1.5 mL were removed]. Be sure to take this into account in your calculation. Compare this to #2. Is there good agreement?