Experiment 5

ELECTROLYSIS

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PURPOSE

Electrolysis is used to force a nonspontaneous oxidation-reduction reaction to occur. The moles of the chemicals which are oxidized and reduced are compared with theoretical yields based on moles of electrons passed through the circuit.

OXIDATION-REDUCTION

Any *spontaneous* oxidation-reduction reaction can be viewed as the chemical being oxidized willingly giving electrons to the chemical being reduced. If the chemicals are arranged so that the electrons must flow through an external wire, a so-called *Voltaic cell* results. As the electrons journey from the oxidation site (anode) to the reduction site (cathode), they can be made to light your flashlight bulb, play your radio, start your car, etc. Because electrons cannot be created or destroyed, the moles of electrons used in the oxidation must equal the moles of electrons used in the reduction.

A similar setup can be used to force a nonspontaneous oxidation-reduction reaction to occur, *if* a source of electric current is placed in the circuit. The external power supply can be thought of as an "electron pump." It can draw electrons away from a chemical that is normally reluctant to lose them (be oxidized), and force electrons onto a chemical that is reluctant to gain them (be reduced). This arrangement is called an *electrolytic cell*, and the process is called *electrolysis.*

Electrolysis is of tremendous practical importance. For example, it is used to produce metals such as aluminum, magnesium, and sodium and other important compounds such as hydrogen gas, chlorine gas, and sodium hydroxide. Approximately 5% of all the electricity generated in the U.S. goes into aluminum production! (Recycling aluminum cans saves an additional 1%.) Another important application of electrolysis is in electroplating where a thin layer of one metal is placed upon a second metal. This can be done for ornamental purposes, such as silver plating, or to protect the metal below, such as chrome plating car bumpers to stop the iron beneath from rusting.

THE ELECTROLYTIC CELL TO BE STUDIED

A simple electrolytic cell will be constructed consisting of two electrodes immersed in dilute sulfuric acid. A power supply will push electrons from the anode to the cathode. Obviously some chemical at the anode must give up electrons. None of the species in the solution (H^+, HSO_4^-, SO_4^{2-}, H_2O) are as easy to oxidize as the copper electrode itself, so the following oxidation half-reaction occurs:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^- \qquad (1)$$
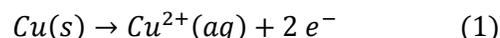
The copper electrode will lose a measurable amount of weight as it oxidizes, and you will see the solution turn blue as $Cu^{2+}(aq)$ forms. From

half-reaction (1) it is clear that each mole of copper oxidized generates 2 moles of electrons.

The electrons being crowded onto the cathode will hop onto the most receptive (easily reduced) chemical they contact. That turns out to be the $H^+(aq)$ ions from the sulfuric acid, resulting in the following reduction half-reaction:

$$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g) \qquad (2)$$
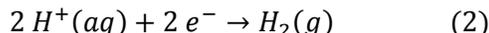
The hydrogen gas will be easily visible as a stream of bubbles coming off of the electrode. The volume of the gas can be measured by having the bubbles displace water from an inverted buret. The moles of H_2 can then be computed using the ideal gas law, $PV = nRT$, after correcting the pressure for the height of the water column and the vapor pressure of water. The moles of $H_2(g)$ produced at the cathode is related to the moles of electrons passed through the circuit by the same 1:2 ratio seen for copper oxidation at the anode.

The total charge passed through the circuit can be determined by measuring the current flow for a known amount of time. Since a current of 1 ampere (A) corresponds to a charge of 1 coulomb (C) passing through the circuit each second, the charge is simply:

$$charge(C) = current(A) \; x \; time(s) \qquad (3)$$

The charge of one mole of electrons is given by Faraday's constant F = 96,500 C/mol. So, the number of moles of electrons can be determined by dividing the total charge by F.

$$n_{electron} = \frac{C}{F} = \frac{A \cdot s}{F} \qquad (4)$$

IN THIS EXPERIMENT

An electric current will be forced through a dilute sulfuric acid solution. The number of moles of electrons will be determined by measuring the amount of current run through the sample during a known time interval. The volume of the hydrogen gas collected at the cathode and the mass of the Cu lost at the anode will each be measured and used to calculate the moles of product formed. Each of these quantities will be compared to the result expected based on the number of moles of electrons.

PRE-LABORATORY PREPARATION

1. Read the procedure and data analysis sections of the experiment.

2. Complete the computer-generated PRELAB assignment. Refer to the procedure and data analysis sections as needed. The prelab questions for this experiment exactly replicate the questions in the data analysis section. Additionally, question 0 is used to calculate how one solution is prepared.

EXPERIMENTAL SECTION

REAGENTS PROVIDED

Sulfuric acid, 1.00 *M*.
Wires, power supplies, burets, and electrodes should be available on the front bench.

HAZARDOUS CHEMICALS

Wash your hands if they come into contact with the sulfuric acid solutions.

WASTE DISPOSAL

All of the chemicals used in this experiment should go in the designated waste containers.

SPECIAL EQUIPMENT

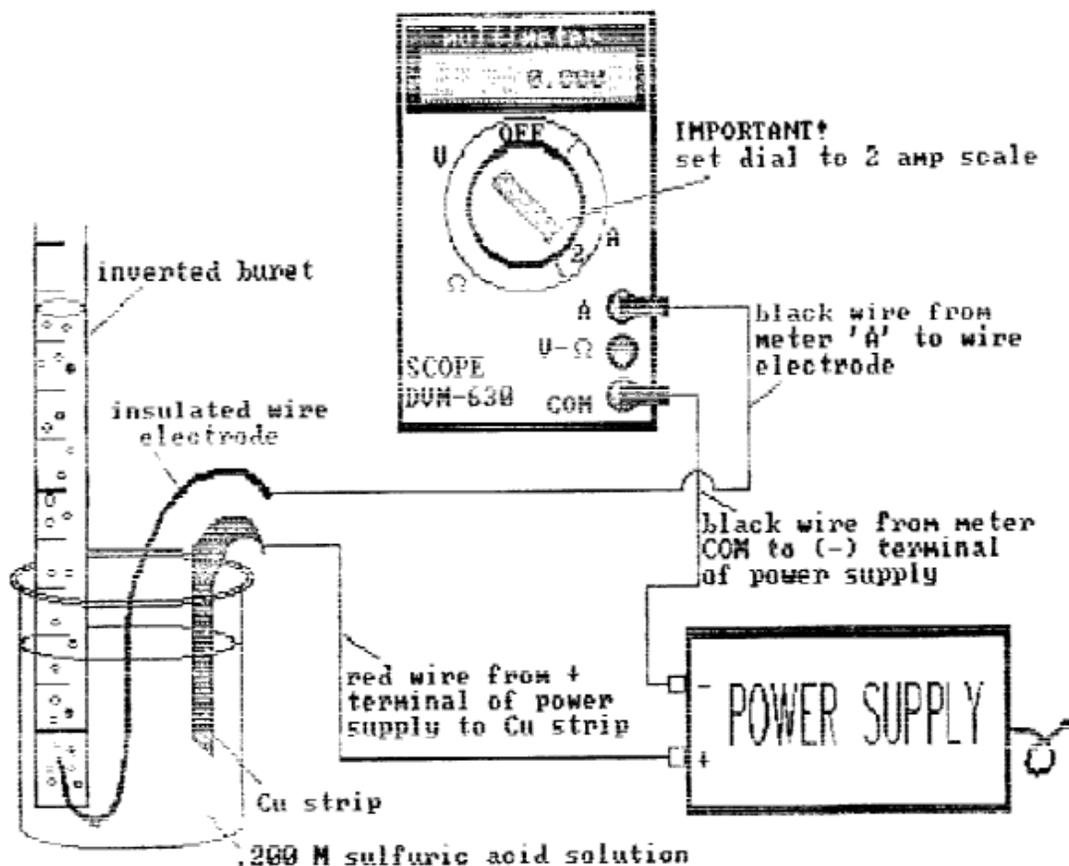You will need the following item:
  1 multimeter

Figure 1.   Circuit arrangement for electrolysis.   The white-striped wire from the transformer connects directly to the solid copper electrode, the bottom of which is also immersed in the solution in the beaker. The black wire from the transformer connects to the negative terminal of the multimeter.   The multimeter is set to 2 A. The positive terminal of the multimeter connects to the insulated wire electrode.

PROCEDURE

Ordinarily, you will work with a partner.

SOLUTION PREPARATION

1. Prepare 150 mL of approximately 0.20 M sulfuric acid, H_2SO_4.

In a 250 mL beaker, dilute the amount of 1.0 M H_2SO_4 stock solution calculated in the prelab.

2. Set up a buret in your solution with one exposed end of an insulated wire electrode <u>completely</u> inside the buret (see Figure 1).

Use a ring stand and buret clamp to fix a 50 mL buret UPSIDE DOWN so that the bottom end (normally the top) of the buret is submerged below the surface of the sulfuric acid, but not resting on the bottom of the beaker.

3. Fill the buret with sulfuric acid.

Open the stopcock on the buret and use a rubber suction bulb on the tip of the buret to draw solution up into the buret until the meniscus is about an inch above the topmost graduation line.   Then close the stopcock to retain the column of solution.   The liquid level in the buret should remain constant.

CIRCUIT PREPARATION

4. Place the solid copper strip electrode in the solution and configure the circuit as shown in Figure 1.

The clips used to attach circuit wires to the electrodes should not be touching the liquid. The positive lead on the power supply is the one with the white stripe.

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Have an instructor check your setup BEFORE you plug in the power supply.

5. Test your circuit.

After your setup has been approved, plug in the power supply. You should see bubbles of gas being released at the exposed wire inside the buret. *All of the gas bubbles must be captured by the buret.* The current reading on the ammeter should be between 0.3 and 0.5 *A*. Current can be adjusted by varying the height of the wire inside the buret.

When you are sure that the apparatus is functioning properly, unplug the power supply.

DATA COLLECTION

6. Refill the buret.

Check the level of the meniscus in the buret. If it has dropped more than 5 mL below the 50 mL line, refill it to the 50-mL line, or slightly below. Record the initial buret reading to the nearest 0.01 mL (remember it is upside-down).

7. Weigh the Cu anode.

Remove the Cu strip anode from the solution. *Handle the Cu strip anode very carefully as some of them have sharp edges!* If it is discolored, dry it and use sandpaper to obtain a clean surface. Rinse it with water and dry it thoroughly. Record the mass of the clean, dry electrode. Return the electrode to the solution and reattach the wire from the power supply.

8. Plug in the power supply and begin collecting data.

The instant the power supply is plugged in will be considered time 0. <u>Record the current reading</u> at this time and then every 30 seconds until about 40-45 mL of gas have been collected (leaving 5 to 10 mL of liquid in the buret). It is very important that you take readings at regular time intervals since the current often fluctuates during the reaction (which is normal). If your readings are equally spaced then it will be sufficient to take an average of the readings during data analysis (since all points correspond to an equivalent time interval).

9. After about 40-45 mL of gas have been collected, record your last data point as you pull the plug to stop the electrolysis. Turn off the multimeter.

10. After the bubbling stops, record the final buret reading (to the nearest 0.01 mL).

11. Use a ruler to measure and record the distance in mm from the meniscus in the buret to the top of the liquid in the beaker.

Do not insert the ruler into the sulfuric acid. It is better to leave the ruler outside the beaker, but as close as possible to the buret.

This will be used to correct the pressure of the gas in the buret for the hydrostatic pressure of the remaining column of liquid.

12. Measure and record the temperature of the gas collected and the lab's barometric pressure.

Assume the temperature of the gas is the same as the surrounding room temperature. Temperature and pressure probes are available.

13. Remove the Cu anode from the solution. Rinse it with water and dry it, as before, but do *not* sand it. Weigh it and record its mass.

14. Open the stopcock to drain the buret into the beaker. Dispose of the solution in the appropriate waste bottle in the hood.

15. Rinse off the wire electrode and then dry it. Wash and store your glassware. Wash your hands thoroughly before leaving lab.

Table 1. *Vapor pressure of water at various Temperatures*

Temperature (°C)	Pressure (mm Hg)	Temperature (°C)	Pressure (mm Hg)
16	13.6	22	19.8
17	14.5	23	21.1
18	15.5	24	22.4
19	16.5	25	23.8
20	17.5	26	25.2
21	18.7	27	26.7

_____   _____   _____
Name   Station Used   Instructor/Day/Time

_____   _____
Partner   Station Checked & Approved

DATA SHEET

Record your measured values with correct units and the appropriate number of significant figures.

Initial: meniscus level _____   mass of Cu anode _____

time	*current*	*time*	*current*	*time*	*current*
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
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_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____

Final: meniscus level _____   mass of Cu anode _____

height of remaining column of liquid _____

room temperature _____   barometric pressure _____

DATA ANALYSIS

As always, calculations should be clearly organized; use proper significant figures, and include the units.

1. Determine the number of moles of electrons that passed through the circuit.

(a) Determine the total charge passed through the circuit. Review your current vs. time data. If you took current readings every 30 seconds or the current was relatively constant, then the total charge is simply the product of the total time (in seconds) and the average current (in amperes). If you *did not* take readings at constant time intervals and the current fluctuated considerably, then to obtain the total charge you must calculate the charge during *each* time interval and sum over all time intervals. The current within a particular time interval is simply the average current over that time interval multiplied by the length of the time interval.

total charge passed through circuit _____

(b) Determine the number of moles of electrons that passed through the circuit by dividing the total charge by Faraday's constant.

number of moles of electrons _____

2. Determine the expected number of moles reacted, based upon the number of moles of electrons passed through the circuit and the number of moles of electrons transferred in the balanced redox reaction.

(a) Determine the expected number of moles of $H_2(g)$.

expected number of moles of hydrogen gas _____

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(b) Determine the expected number of moles of copper oxidized.

expected number of moles of Cu(s) oxidized _____

3. Determine the number of moles of hydrogen gas produced.

(a) Use the initial and final meniscus levels to determine the volume of the hydrogen gas collected.

volume of gas collected _____

(b) This data, along with the temperature of the gas and its pressure, may be used to calculate the number of moles present using the ideal gas law: $PV = nRT$, where $R = 0.0821$ L atm mol^{-1} K^{-1}. The pressure of the gas collected is the barometric pressure of the room corrected for the equilibrium vapor pressure of water (since the gas is collected over water and it is assumed to be saturated with water vapor) and for the hydrostatic pressure of the column of liquid remaining in the buret. The pressure of the hydrogen gas may be calculated as follows:

$$P_{H_2} = P_{barometric} - P_{hydrostatic} - P_{H_2O}$$

where

$$P_{hydrostatic} = \frac{height\ of\ liquid\ in\ buret\ (in\ mm)}{13.6\ mm\ H_2O/\ mm\ Hg}$$

and P_{H_2O} can be found in Table 1.

pressure of hydrogen gas collected _____

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(c) Use the ideal gas law to calculate the number of moles of hydrogen. Be sure you convert volume and pressure into appropriate units.

number of moles of hydrogen gas formed _____

4. Determine the actual number of moles of copper oxidized. Use the initial and final masses of the Cu anode and the molar mass of Cu.

number of moles of copper oxidized _____

5. Calculate the "electrochemical" percent yield.

$$percent\ yield = \frac{actual\ number\ of\ moles}{"expected\ number\ of\ moles"}\ x\ 100\%$$

(a) Calculate the percent yield of $H_2(g)$ produced.

percent yield of $H_2(g)$ production _____

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(b) Calculate the percent yield of Cu(s) oxidized.

percent yield of Cu(s) oxidation _____

6. If your yields are not exactly 100%, discuss what you think are the most logical or likely explanations.