

Electrochemistry – Determination of Avogadro's Number and Faraday's Constant

Objective: To observe the voltage produced when two chemical cells are combined to produce a battery and to determine which cell contains an oxidation reaction and which has a reduction reaction. To experimentally determine Avogadro's number and Faraday's constant by electrolysis of copper.

Concept to be Tested: When two different metals are in contact with each other, one tends to spontaneously lose electrons to the other. This electric potential can be measured in volts. It is possible to use an electrolytic cell to experimentally determine Avogadro's number and Faraday's constant.

Text References: McMurray and Fay: Chapter 17.1-17.19

Introduction

Batteries, computers, hard disks, jump drives, floppy disks, and even our own nervous system are examples of electrochemistry in action. The term "action" is a bit misleading since these are based upon potential energy. This potential energy is measured in volts. Electricity and electrochemistry have their own vocabulary and it is perhaps wise to review these definitions, as they will pertain to this experiment.

ampere – also known as **amp**, abbreviation **A**, the ampere is the SI unit of current and is defined as the charge carried by a current at the rate of one coulomb per second.

coulomb – abbreviation **C**, the coulomb is the SI unit of electric charge and is defined as the amount of electric charge carried by a current of one amp per second. A coulomb can also be defined in terms of electric charge and is equal to exactly 6.241×10^{18} elementary charges.

electromotive force – also known as **emf**, abbreviation ξ , the voltage difference between electrodes, measured in volts.

electron – a subatomic particle that carries the charge of -1.602×10^{-19} C

volt – abbreviation **V**, the volt is the SI unit of electric potential. Electric potential is defined as the amount of potential energy present per unit charge. One volt represents a potential of one joule per coulomb of charge.

watt – abbreviation **W**, is the SI unit of power. Power is the rate at which work is done or equivalently, the rate at which energy is expended. One watt is equal to a power rate of one joule (of work) per second. This unit is used in both mechanics and electricity and links mechanical and electrical units to each other. In

electrical terms, the watt is the power produced by a current of one ampere flowing through an electric potential of one volt.

The experiment today will be in two parts, both an electrochemical (voltaic or galvanic) experiment and an electrolytic experiment. The electrochemical experiment will involve measuring the potential that exists between two metal/metal ion cells. You will determine which cell is the reducing cell and which is the oxidizing cell. You will also compare the values you obtain for the potential between your half-cells and the potential calculated for this pair of half-cells using standard reduction reference tables. The electrolytic portion of the experiment will involve the electrolysis of copper. You will determine the average current and also measure the amount of metal lost. By determining the average current and the time of the electrolysis, you can calculate the coulombs that were involved in the electrolysis. This coupled with the amount of metal lost by the anode will allow you to experimentally determine both Faraday's constant and Avogadro's number and calculate your experimental error.

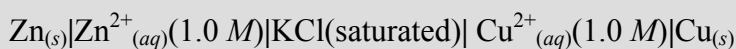
Electrochemical Cells

FYI. We tend to use the terms voltaic and galvanic interchangeably. It is probably much more correct to describe this type of cell as an electrochemical cell in which the difference in electromotive force is measured in volts. Galvanic cells are often pictured as two separate solutions of electrolytes connected by a salt bridge – these are identical to cells called voltaic cells. Galvanic cells get their name from Luigi Galvani who connected two different types of metal and then touched these to different ends of a nerve in a frog's leg and observed "animal electricity." Voltaic cells get their name from Alessandro Volta who stacked alternating pairs of metals each separated by a salt water soaked piece of cloth. Volta's device was known as a voltaic pile which today would be called a (crude) battery. Regardless of the name, a spontaneous reaction will occur in this type of cell and electrons will flow from the anode to the cathode.

Oxidation-reduction reactions involve a transfer of electrons. In a spontaneous redox reaction, electrons flow from the oxidizing reactant (reducing agent) to the reducing reactant (oxidizing agent). If the two half-reactions, oxidizing reaction and reducing reaction, can be separated, this flow of electrons can be directed through a wire rather than happening at the interface of the two reactants. An **electrochemical cell** (voltaic or galvanic cell) is this type of device (a battery). In the experiment you will perform today, the two half-reactions of an oxidation-reduction reaction are physically separated so that the electron transfer has to occur through a wire rather than by direct contact.

As you are probably aware, you must have a complete circuit *before* you can get an electric current. Unfortunately, in this case a second piece of wire will not work to complete the circuit. While we tend to concentrate on the electrons running through the wire portion of the circuit, after all this is what we're using the battery for, ions are being generated or consumed at the respective electrode surfaces. Unless an appropriate counter ion can be supplied (or removed) to balance the charge, the electron flow stops.

A **cell diagram** of an electrochemical cell lists each part of the cell, from the anode (on the left) to the cathode (on the right), using the symbol | to indicate separate phases. For a typical standard ZnCu cell that had a KCl salt bridge this would be written as:



Generally the details of the salt bridge are omitted so the cell diagram is typically written as:



As a result, the salt bridge usually shows up in these diagrams simply as ||.

A salt bridge allows ions to freely move between one half-cell and the other. Again, freely may imply a bit too much freedom of movement here. A typical salt bridge is a gel or agar filled tube. The gel or agar is viscous enough to remain in the tube and was made using a neutral salt solution (the concentrations of this salt solution typically range from 5% to saturated). This **neutral** salt solution is a salt that will not be oxidized or reduced in the electrochemical cell being studied. Typically this neutral salt is KNO_3 , KCl , NaCl , or a related salt. As the electrons travel from one side of the electrochemical cell (the anode) to the other (cathode) a charge imbalance would be created. The salt bridge allows the anions to be transferred from one side to the other. At the same time, the salt bridge prevents the contents of one cell from mixing with the other. The salt bridge you use today will be either a narrow strip of paper towel, a strip of filter paper, or a piece of string that is moistened with an aqueous solution of KNO_3 . This will efficiently complete the circuit. You will add the salt bridge to your cell just before measuring the voltage. Since your electrochemical cell will only be 'run' for a few moments to determine the voltage generated, no mixing of the two solutions is expected.

In this experiment you will construct and evaluate several voltaic cells. The voltage differential between the electrodes is called the electromotive force, emf, and is measured in volts. You can treat each half cell as if it has its own electrochemical potential and so the cell emf is equal to the sum of the half-cell emfs. You will need to compare the value that you obtain experimentally from your constructed cell with the value that you calculate for a standard cell. Chances are fairly certain that you will not have created a standard cell. Even if your cell was standard, after allowing current to flow for a few moments will alter the concentrations within the two half-cells and the electrochemical cell would no longer be standard.

Fortunately, the Nernst Equation allows you to examine what happens to the relative cell potential as its concentration is changed relative to the other cell. Of course, it is possible to take advantage of the relationship shown in the Nernst equation to minimize the effect seen in your experiment.

The Nernst Equation is named after the German physical chemist Walther Nernst who was first to formulate it. Nernst expressed his equation in terms of relative activities of the components of the cell. It was this same research into chemical activities that led to his other discoveries including the expression of K_{sp} , the development of the pH meter and other devices relying on electrode potentials.

The Nernst Equation is shown here:

$$E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Oxid}]}$$

It is possible to use the Nernst equation to our advantage. First by choosing metal ions that transfer the same number of electrons, the concentrations of the reduced species and oxidized species will be treated the same. That is, their concentrations will be raised to the same power (in this case 1) in the Nernst equation. Then by starting with the same concentration **regardless of the magnitude of that concentration**, the concentrations cancel out. This means that RT/nF is multiplied by the logarithm of 1, which is **zero**. In short, by using the Nernst equation, it is possible, at least for a limited period of time to have $E = E^0$. You will be using solutions that are 0.1 *M*. These will produce the same voltage potential as a standard cell. The 0.1 *M* solution is much less hazardous than the 1.0 *M* solution.

Before going on, it should also be pointed out that E depends upon the **concentration** of the various ions **not the quantity** of solution present. The standard reduction potential is an intensive property of the half-cell **not** an extensive property. **Therefore you will get the same voltage reading regardless of the volume of solution you use.**

Once the circuit is complete, electrons will spontaneously flow from the anode to the cathode. To measure the potential, it is necessary to have a multimeter (switched to function as a voltmeter) as part of the circuit. A guide to the construction of this circuit will be given in the Experimental Procedure section.

Determination of Avogadro's Number and Faraday's Constant

In this part of the experiment you will use an electrolytic cell to determine Avogadro's number. Since Faraday's constant is Avogadro's number times the charge on an electron, you will also determine Faraday's constant using your experimental data.

An **electrolytic cell** is a **nonspontaneous** process. In this, electricity is used to force a nonspontaneous reaction to occur. The use of an electrolytic cell is generally called **electrolysis**. Evidence exists that electrolysis has been practiced for well over 2000 years. There are numerous examples of an object made of a base metal (relatively inexpensive or common metal) being coated with a more valuable metal such as gold.

Today you will use electrolysis to experimentally determine Avogadro's number. To do this it will be necessary to use the multimeter as an ammeter. This will require switching the voltage lead to the 10 Amp connection. Specific directions for "wiring" your circuit with the ammeter for the electrolysis will be given in the experimental section. You will need to record the amperage every minute in order to determine the average amperage for the duration of the experiment. The current will probably remain fairly constant unless you are using a weak battery.

An **ammeter** is a measuring instrument used to measure the flow of electric current in a circuit. Electric currents are measured in amperes, hence the name. The word “ammeter” is commonly misspelled as ameter or mispronounced as “ampmeter.”

To perform your electrolysis, you will need two copper electrodes, a 9-volt battery, and a solution of electrolyte (among other things). Since all of the copper “lost” by the anode should (in theory) be gained by the cathode, none of the copper is expected to remain in the solution. Therefore it should be possible to run the electrolysis in just about any type of electrolyte. One common electrolyte used for this experiment is dilute sulfuric acid. Dilute sulfuric acid is very corrosive and considering that the cell will get hot during the electrolysis, hot dilute sulfuric acid is even more corrosive. Because of this, you will be running your electrolysis in a copper sulfate solution. This is also an excellent electrolytic solution for this electrolysis and it is much less hazardous. You will be directed on how to set up your electrolysis so that the copper sulfate solution can be reused.

During the electrolysis, the anode will lose mass and the cathode will gain mass. Generally, you might want to measure how much mass the cathode gains. In theory, this is logical. In practice, you will discover that much of the copper that is plated onto your cathode is present as a fragile black powder. The fine metal (copper) powder produced on the cathode diffracts light rather than reflects it so the surface of the cathode generally appears black following electrolysis. This powdery surface is very fragile and a significant amount is usually lost during handling. You need a fairly accurate measurement of the amount of metal deposited during your experiment. Remember, the mass gained by the cathode is equal to the mass lost by the anode. Therefore, it is possible to get a very good reading of the amount of metal lost by the anode.

Data Collection and Calculations

Electrochemical Cells. Data collection for the electrochemical cells is fairly easy. The two half-cells are created (**using a minimum quantity of solution**) and the electrodes are attached to the voltmeter (set to **2 V** direct current – this is the V with what appears to be an equal sign (=) above it or a single solid line (–), alternating current uses a ~ over the V). The red lead is the “cathode” and should be plugged into the V/ Ω port on the multimeter, the black lead is the “anode” and should be plugged into the COMM (or COM) port. When you clip the electrode to the probe of the voltmeter, you are arbitrarily predicting which half-cell is the reducing cell and which is the oxidizing cell. **If you have chosen correctly, when the circuit is completed you will see a positive voltage. A negative voltage means that the cells are “reversed.”** **THE MAGNITUDE OF THE VOLTAGE IS CONSTANT only the sign changes.** Should you get a negative voltage when measuring one of your electrochemical cells it means that the electrode on the black lead is really the cathode of the cell you created. You do not need to re-run the measurement. You will compare the voltage that you read from your cell to the voltage that you calculate using Standard Reduction Potential Tables (from OWL or your textbook).

Electrolytic Cell. Data collection here is also fairly simple. You will need a stopwatch and you must start the stopwatch either when you complete the circuit by the final connection to the battery **OR** when you place the final electrode into the solution. The instant the circuit is complete electrons will begin flowing. Record the amperage at 1.00 minute intervals. The average amperage is determined by adding all of the amp readings together and dividing by the total readings (you want the average). You will need to run the electrolysis for at least 17.00 min. Record the time and amperage just before breaking the circuit.

You will need to reconfigure the multimeter so that it will measure amps for this experiment and then construct the wiring scheme so that the ammeter is part of your circuit (this will be shown in the Experimental section). You will need to determine the mass of the anode before you begin the experiment. **Which electrode will be the anode in your setup?** Actually an excellent question; and the simple answer is you probably don't know. This is not to impugn your expertise, but a single swapped connection reverses the identities of the two electrodes. Therefore, clean and weigh **both electrodes** before beginning the electrolysis. Make certain that you can distinguish between the two electrodes; **the anode will be the shiny electrode at the end of the experiment.** You can then reweigh that electrode and determine how much copper was lost.

As far as the calculations go, it is probably best to demonstrate these using an example.

Example. An electrolytic cell of two copper electrodes in a 1 M CuSO₄ solution was run for 30.00 min. The average current was determined to be 0.601 amps. When compared to its starting mass, the anode lost 0.3554 g of Cu during the electrolysis. Calculate Avogadro's number using this data. Calculate Faraday's constant from this data. What is the experimental error associated with each value?

First determine the total charge that passed through the electrolytic cell. Remember you must use seconds in your calculation.

$$30.00 \text{ min} \times \frac{60 \text{ sec}}{1 \text{ min}} \times 0.601 \text{ amp} = 1082 \text{ coulomb}$$

Now calculate the number of electrons in the electrolysis by using the charge on 1 electron (use the magnitude of the charge on the electron not the sign).

$$1082 \text{ C} \times \frac{1 \text{ electron}}{1.6022 \times 10^{-19} \text{ C}} = 6.753 \times 10^{21} \text{ electrons}$$

Now determine the number of copper atoms lost from the anode. The electrolysis 'consumes' two electrons per Cu²⁺ formed. Therefore the number of Cu²⁺ ions formed is equal to half the number of electrons.

$$\text{number Cu}^{2+} \text{ ions} = 6.753 \times 10^{21} \text{ electrons} \times \frac{1 \text{ Cu}^{2+}}{2 \text{ electrons}} = 3.376 \times 10^{21} \text{ Cu}^{2+} \text{ ions}$$

Now calculate the number of copper ions per gram of Cu. The mass of the electrons is so small that it is negligible, so the mass of Cu^{2+} equals mass of Cu lost.

$$\text{number Cu}^{2+} \text{ ions/g} = \frac{3.376 \times 10^{21} \text{ Cu}^{2+} \text{ ions}}{0.3554 \text{ g Cu lost}} = 9.500 \times 10^{21} \text{ Cu}^{2+}/\text{g}$$

$$9.500 \times 10^{21} \text{ Cu}^{2+}/\text{g} = 9.500 \times 10^{21} \text{ Cu atoms/g}$$

Finally to calculate Avogadro's number multiply the atoms/g value you obtain in this calculation by the atomic weight of Cu.

$$\text{Avogadro's number} = \frac{9.500 \times 10^{21} \text{ Cu atoms}}{\text{grams}} \times \frac{63.546 \text{ g Cu}}{\text{mol Cu}} = 6.040 \times 10^{23} \text{ atom/mol}$$

Calculate the percent error in this number before working on Faraday's number. Look at the magnitude of the error (don't worry about the sign of the error – to high or too low).

$$6.04 \times 10^{23} \text{ atom/mol}_{\text{exper.}} - 6.02 \times 10^{23} \text{ atom/mol} = 0.02 \times 10^{23} \text{ atom/mol}$$

$$\% \text{ Error Avogadro's number} = \frac{0.02 \times 10^{23} \text{ atom/mol}}{6.02 \times 10^{23} \text{ atom/mol}} \times 100\% = 0.3\%$$

Now for the calculation of Faraday's number. Faraday's number is simply the charge on an electron times Avogadro's number.

$$\text{Faraday's number} = 6.04 \times 10^{23} \text{ electron/mol}_{\text{exper.}} \times 1.6022 \times 10^{-19} \text{ C} = 96883 \text{ C}$$

$$\text{Difference from accepted value} = 96833 \text{ C} - 96485 \text{ C} = 288 \text{ C}$$

$$\% \text{ Error Avogadro's number} = \frac{288 \text{ C}}{96485 \text{ C}} \times 100\% = 0.3\%$$

Experimental Procedure

You will need to obtain a multimeter (with red and black leads), three sets of alligator clamp connectors (a wire with alligator clamps attached to both ends), a working stop watch, a 6-volt battery, at least 10 small containers (small plastic cups will be used instead of beakers), 10 narrow strips of filter paper or paper towel (~7 cm or ~2.5" long), and a plastic transfer pipet. You will also need two (2) copper electrodes, one lead (Pb) electrode, one nickel (Ni) electrode, one tin (Sn) electrode, one zinc (Zn) and one iron (Fe) electrode. You will also need a small beaker with a few mL of KNO_3 solution (very little will be needed).

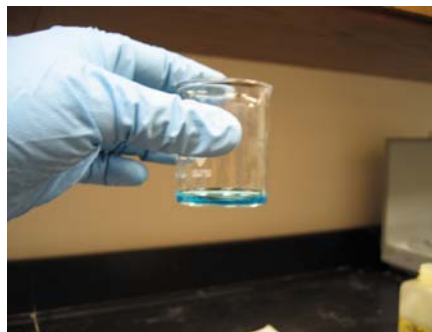
Electrochemical Experiment



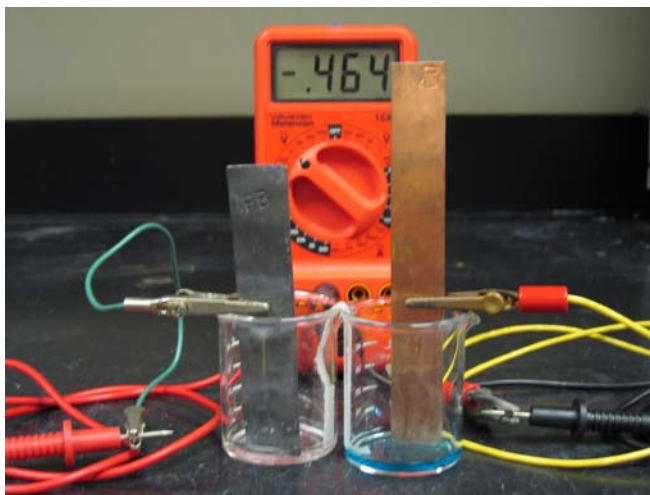
You will construct and measure the voltage of ten (10) different electrochemical cells. To do this you will need to configure the multimeter to measure voltage. First you will need to make certain that the probes are connected to the correct slots. Place the red lead in the V/ Ω slot, the black lead should be in the COM (or COMM) port. **Set the dial to 2 V.** This setting should be sufficient to measure all of your electrochemical cell potentials. The red lead is your “cathode” while the black lead will be interpreted as the “anode” by the volt meter. A positive reading means that the half-cells are arranged in the proper configuration. **A negative reading** means that the cell that is attached to the black lead is actually acting as the cathode. Note this on your data sheet. You do not need to re-run this cell; the magnitude of the voltage will remain the same.

The negative sign means that the electrons are flowing opposite to the direction you have the cell constructed.

To construct each half-cell you will take a small container (plastic dose cup, etc.) and obtain a small quantity of one of the solutions. The picture to the left shows a beaker that has **more** solution than is needed (**use less** if possible). Once you select a solution for a container, you will use an electrode that matches the cation (*e.g.*, copper electrode with a Cu^{2+} solution).



You will now need to connect the voltmeter to the electrodes and you will do this by clamping the electrode to the probe by using an alligator clamp. Place each electrode into the appropriate solution and then drape the strip of filter paper or paper towel between the two containers. A piece of paper towel is used here. Notice how the towel makes contact with both solutions. **NOW** use the plastic transfer pipet to drip KNO_3 solution onto the top of the string or strip of paper towel. This will dampen the



“salt bridge.” When the ‘dampness’ contacts both liquid surfaces you will obtain a voltage across the cell. Notice that the voltage shown in this picture is **negative**. This means that the $\text{Cu}|\text{Cu}^{2+}$ cell that is connected to the black probe is actually the cathode of the reaction and electrons are flowing to this cell. The $\text{Pb}|\text{Pb}^{2+}$ cell is the anode (electrons are flowing from the $\text{Pb}|\text{Pb}^{2+}$ cell to the $\text{Cu}|\text{Cu}^{2+}$ cell). The potential between this cell is 0.484 V. If the cells were swapped (the $\text{Cu}|\text{Cu}^{2+}$ cell connected to the red probe), the voltage would remain the same but be positive.

If there are a sufficient number of containers, you should be able to have several “half-cells” ready so that all that will be needed is to swap electrodes and use a new salt bridge. This way you can rapidly progress through the 10 different electrochemical cells. Having your notebook prepared will also speed up this part of the experiment.

Obtain the voltage reading and record this reading along with the cell construction in your notebook. Remove the salt bridge, discard the solutions into the waste container, and rinse and dry the electrodes. Discard the used ‘salt bridge’ in a beaker provided for this purpose in the hood. Then construct another cell. **DO NOT REUSE THE SOLUTION FOR A SECOND ELECTROCHEMICAL CELL.**

Construct ten (10) different combinations of half-cells and measure the voltage generated by each combination. Indicate how each cell was constructed (anode, cathode) and then indicate which electrode was actually the cathode. Discard the solutions in the appropriate waste bottles. Discard the used “salt bridges” in a beaker provided for this purpose.

Determination of Avogadro’s Number and Faraday’s Constant

You will need a 250-mL beaker, the multimeter, a stopwatch, the two copper electrodes, the 6-Volt battery, and 3 sets of alligator clamps. Rinse the beaker several times with distilled water and dry it thoroughly. Place ~ 150 mL of the 1.0 M CuSO_4 into the

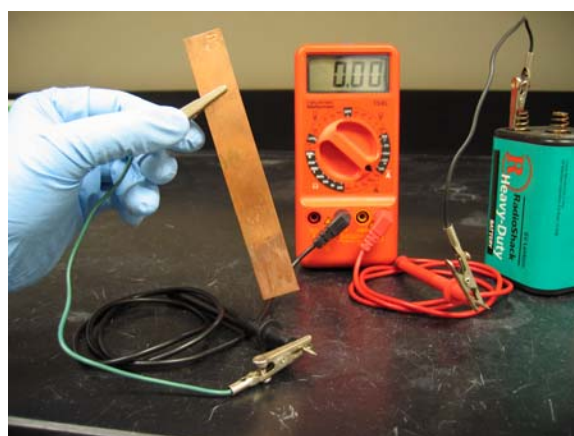
beaker. This is your electrolytic solution. Clean and dry both copper electrodes. Make certain that you can tell the two electrodes apart and then determine the weight of each electrode to four (4) decimal places.

Now you will need to configure your multimeter to convert it into the ammeter mode. This is done by moving the red probe from the V/ Ω slot to the 10 A slot. Set the dial to the 10 A position. Do not be alarmed if the multimeter beeps or whistles as you are moving either the probe or the dial. This configures to multimeter into the ammeter mode. (The multimeter is pictured upright to show the position of the probes; you may lay it flat on the bench if you choose to do so.) The following set of instructions and pictures should aid in setting up your experimental apparatus.

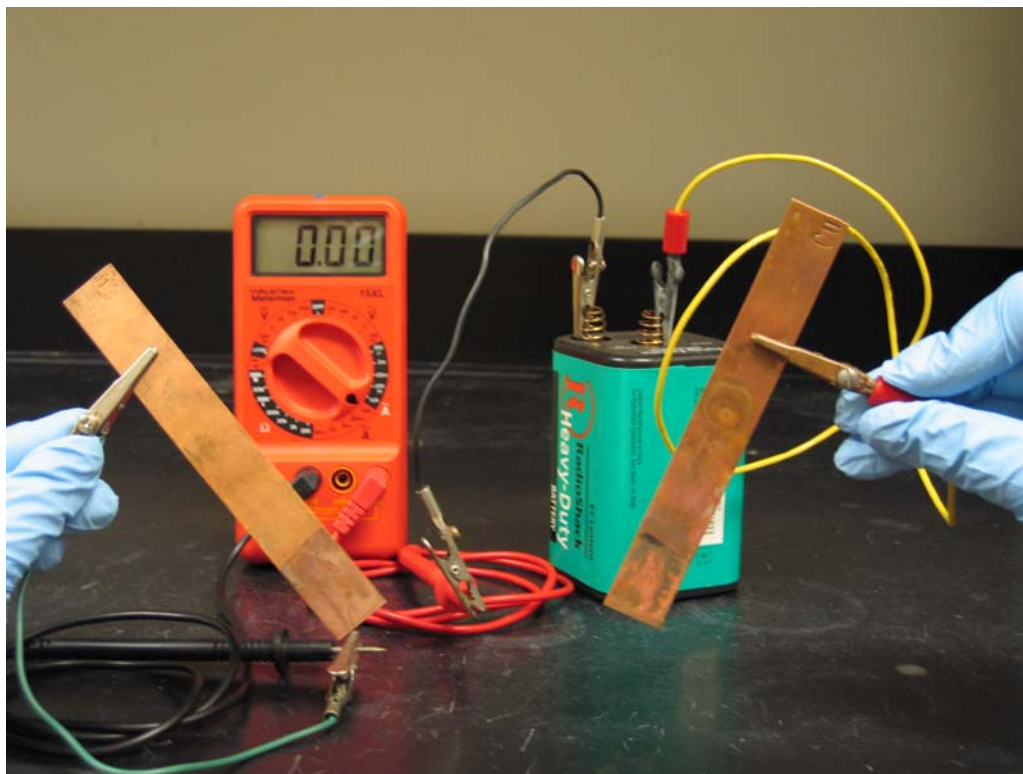


Connect the red probe to the outer (edge of battery) terminal by using one set of alligator clamps

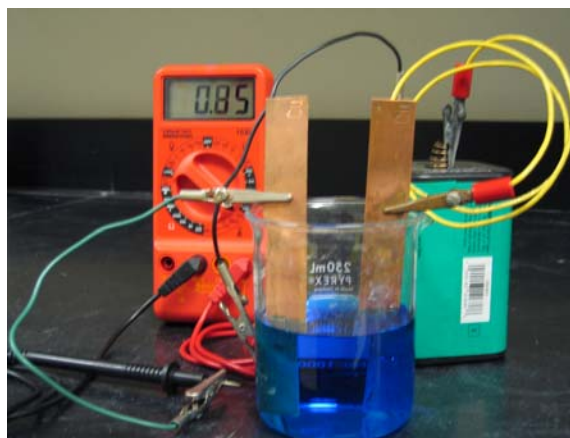
Connect the black probe directly to one of the copper electrodes. Be certain to know which of the two copper electrodes is connected here and make certain you have its weight recorded.



Now connect the central terminal of the battery to the other electrode. **DO NOT allow the electrodes to touch.** No current will flow until you complete the circuit. Be ready to begin timing when you place the electrodes in the beaker of electrolyte solution.



There will be no current until **both** electrodes are in contact with the liquid. If you wish you may position one electrode in the beaker and then start the stopwatch the instant the second electrode contacts the surface. Record the amperage reading every 60 seconds. You will need to run this electrolysis a minimum of 17 minutes (longer if you have time). [You need at least 4 significant figures for your calculations and 17 minutes is 1020 seconds.]



Disconnect the cell by breaking the circuit. The easiest way to do this is to pull one electrode from the solution (take care not to touch the other electrode). Stop timing the instant the voltage drops during this disconnection. Record the time the electrolysis was running. Rinse each with water and then dry each with a paper towel. Record which electrode was the anode and which the cathode was; red probe (10 A slot) or black probe (COM slot). Weigh and record the mass of the anode.

Cleanup

Disassemble the electrolytic cell. Return the probes to the voltage setting (red probe connected to the V/ Ω port). **Pour the 1 M CuSO₄ solution back into the stock container.** *If* you notice grit or debris on the bottom of the beaker, the last portion (dregs) of the CuSO₄ solution can be discarded into the waste container. This solution can be re-used by other lab sections **if** uncontaminated. Disassemble the rest of the set up. Return the multimeter, alligator clamps, and battery to their appropriate bins. The excess KNO₃ solution can be discarded by pouring down the drain. Collect all used 'salt bridges' and discard them in a beaker in the hood. The 0.1 M solutions used in your electrochemical cells should be discarded in the appropriate waste container in the hood. Rinse all containers thoroughly with water, dry with a paper towel and return to their appropriate bin or storage location.

Safety

Safety glasses must be worn at all times while in the laboratory. All of the electrolytic solutions should be considered to be toxic and corrosive. Even at these relatively low concentrations, accidental ingestion of any of the divalent cations would cause serious abdominal discomfort (cramping) and diarrhea. These solutions must be disposed of in the appropriate waste container. Dispose of the used 'salt bridges' in a beaker in the hood so that they may be placed with solid laboratory waste. Wash your hands before you leave the laboratory.