

## Experiment 21

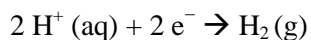
### Voltaic and Electrolytic Cells rev 1/2013

#### INTRODUCTION:

A voltaic cell is a specially prepared system in which an oxidation-reduction reaction occurs spontaneously. The oxidation and reduction half-reactions are separated so that the current must run through an external wire. This spontaneous reaction produces an easily measured electrical potential. Common household batteries are actually voltaic cells.

We can predict the potential for any voltaic cell by using standard reduction potentials that are tabulated in the Appendix of your textbook. The potential of a cell can be calculated by combining the potentials of its half-reactions:  $E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}}$ . But, if you look at the table, you will find that all the reactions are listed as reductions. Which of the two half-reactions in our cell is actually the oxidation? Because spontaneous overall reactions have positive values of  $E$ , we know that the half-reaction with the smaller (more negative) half-potential will actually be an oxidation.

In electrolytical cells, electricity is supplied to drive a nonspontaneous redox chemical reaction. This process is known as electrolysis. As in voltaic cells, the number of electrons required to drive electrolysis is directly related to the number of electrons needed in the reduction half reaction. The reduced species is frequently a metal cation,  $\text{H}^+$ , or water; in this experiment we will reduce  $\text{H}^+$ . Hydrogen gas is produced from the reduction of hydrogen ions

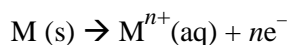


Note that to form one mole of  $\text{H}_2$  gas, two moles of  $\text{H}^+$  are reduced and two moles of electrons are required. One mole of electrons is known as a faraday. This is a fundamental amount of electricity, similar to one mole of atoms being a fundamental amount in chemistry. The “gram equivalent mass” (GEM) of a substance is the amount (in terms of mass) of a given material that reacts with, or releases, one mole of electrons. We can define GEM as the mass of substance per mole of electrons. In the example above, the GEM of  $\text{H}_2$  is 1.008 g, the mass of one mole of  $\text{H}_2$  gas (2.016 g) divided by 2, the number of faradays required to produce one mole of  $\text{H}_2$  gas.

In Parts I and II of this experiment, you will prepare a variety of semi-microscale voltaic cells in a 24-well test plate. A voltaic cell is constructed by using two metal electrodes and solution of their respective salts (e.g., Cu in  $\text{Cu}^{2+}$  or Zn in  $\text{Zn}^{2+}$ ) with known molar concentrations. Note, you will drape a short length of string draping between the two wells to form your cell. This string has been soaked in a solution of  $\text{KNO}_3$  and serves as the salt bridge in our cell, completing the circuit. In lab, how can we tell which half-reaction is the oxidation? When your voltaic cell is set up and has positive value for the cell potential, the black connector wire is attached to the anode, the half-cell in which oxidation is occurring.

In Part I of this experiment, you will use a voltmeter to measure the potential of a voltaic cell with copper and zinc electrodes. You will then test two voltaic cells that have unknown metal electrodes paired with zinc. Through careful measurements of the cell potentials, you will identify the unknown metals (Part II).

In Part III, you will use electrolysis to determine the identity of an unknown metal electrode. To do so, you will construct an electrolytic cell and measure the volume of hydrogen gas produced. Using the ideal gas law, you can find the moles of gas produced and from this, the gram equivalent mass of the metal. In your cell, the following oxidation reaction occurs:

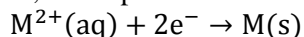


You can use the data you collect to determine the value of  $n$ , the charge on the cation. From this equation, you can see that oxidizing one mole of metal requires  $n$  faradays. In this experiment, you will calculate GEM for your electrode, find its identity in the table below, and using this information determine the charge on the cation.

Table 1. GEM of selected metals	
Metals	GEM (g/mol)
Aluminum	9.0
Copper	31.8
Iron	27.9
Lead	103.6
Tin	59.3
Zinc	32.7

### PRE-LAB ASSIGNMENT:

Copy the table below into your lab notebook. Use the table of standard reduction potentials in your text book to complete the table. For each metal, look up the half-reaction for



Silver is an exception; there you want the  $Ag^{+}$  ion. Decide which half-reaction in each pair must be the oxidation in order to give a positive value of  $E^{\circ}_{cell}$  when the half potentials are added together. An example is provided.

Electrodes	Half-reactions	$E^{\circ}$	Oxidation	$E^{\circ}_{cell}$
Zn Cu	$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$	-0.76 V +0.34 V	Zn	+1.10 V
Zn Pb				
Zn Ag				
Zn Mg				
Zn Ni				

## PROCEDURE:

This procedure will be done in pairs. Record the names of both partners in your lab notebook.

### Part I: Determine the E for a Cu-Zn Voltaic Cell

1. Use a 24-well test plate as your voltaic cell. Use Beral pipets to transfer small amounts of 0.10 M  $\text{Cu}(\text{NO}_3)_2$  and 0.10 M  $\text{Zn}(\text{NO}_3)_2$  solution to two neighboring wells in the test plate.
2. Obtain one Cu and one Zn metal strip to act as electrodes. Polish each strip with steel wool. Place the Cu strip in the well of the  $\text{Cu}(\text{NO}_3)_2$  solution and place the Zn strip in the well of the  $\text{Zn}(\text{NO}_3)_2$  solution. These are the half cells of your Cu-Zn voltaic cell.
3. Make a salt bridge by soaking a short length of string in a beaker that contains a small amount of 1 M  $\text{KNO}_3$  solution. Connect the Cu and Zn half cells with the string as shown in Figure a.
4. Connect the leads from the voltmeter to the Cu and Zn electrodes to get a positive potential reading. (If you see a negative value, reverse the leads.) Record the potential immediately after making the connection. Record with metal was attached to the black connector wire.
5. Remove both electrodes from the solutions. Clean and polish each electrode. Measure the potential again.
6. Repeat for a third time, polishing each electrode and re-measuring the potential.
7. Record the metal attached to the black wire, the potentials from the three trials, and the mean value in a well-labeled data table in your lab notebook.
8. Dispose of the solutions in the waste container provided and return the metals to the supply bench.

### Part II: Determine the E for Two Voltaic Cells Using Zn and Unknown Metals X and Y

9. Obtain a small amount of the unknown electrolyte solution labeled "0.10 M X" and the corresponding metal strip, X. Clean the metal strip with steel wool.
10. Use a Beral pipet to transfer a small amount of 0.10 M X Solution to a well adjacent to the 0.10 M  $\text{Zn}(\text{NO}_3)_2$  solution in the test plate.
11. Make a new salt bridge by soaking a short length of string in the beaker of 1 M  $\text{KNO}_3$  solution. Connect the X and Zn half cells with the string.
12. Measure the potential of the X-Zn voltaic cell three times, following the same general procedure used before, cleaning the metal strips with steel wool each time. Again, record your data and the mean value in a well-labeled table. Be sure to note which metal the black electrode was attached to.
13. Repeat steps 8-11 using the unknown metal strip Y and its corresponding electrolyte solution, 0.10 M Y.
14. Dispose of the solutions in the waste container and return the metals to the supply bench.

### Part III: Determine the Identity of an Unknown Metal by Electrolysis

15. Set up an electrolysis apparatus as shown in Figure 1. Use a ring stand and buret clamp to secure an *inverted* buret over a 150-mL beaker. Carefully bend a piece of insulated copper wire to fit in the beaker with the exposed tip completely inside the open end of the buret. Lower the buret such that the wire is trapped between the buret and the bottom of the beaker. Attach a small length of rubber tubing to the top of the buret. Add 100 mL of 0.5 M  $\text{HC}_2\text{H}_3\text{O}_2$  in 0.5 M  $\text{Na}_2\text{SO}_4$  to the beaker. Use a pipet bulb to draw the solution up the buret to the 50-mL mark. You will need to open the stopcock on the buret

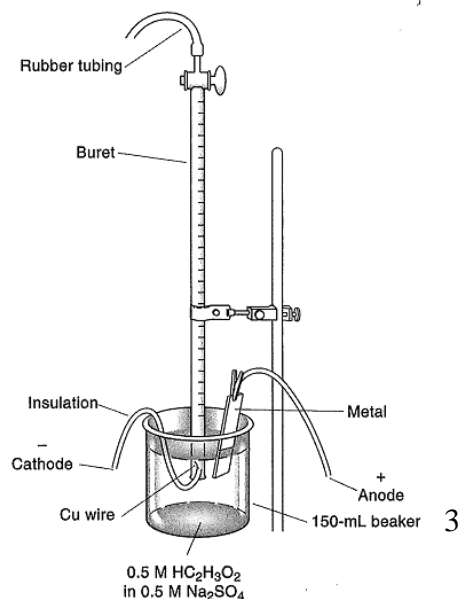


Figure 1. Electrolysis Apparatus

while drawing up the solution. Check the solution level after a few minutes to make sure the buret does not leak. Record the level of the solution in the buret.

16. Obtain an unknown metal electrode from the supply bench. Be sure to record the number of the unknown in your lab notebook. Lightly sand the metal to clean it. Rinse the metal with water and then with acetone. When the acetone has evaporated and the metal is dry, weigh it on an analytical balance. Record the weight to 0.001 g.
17. Setup the cell. Connect the metal electrode to the (+) side of the power source (+ = red) and immerse the metal (*but not the alligator clip*) into the conducting solution. Connect the copper wire to the other side of the power source. This will be the cathode. You should see gas bubbles form immediately.
18. Allow the reaction to continue until you have collected about 20 mL of gas. At that point, stop the reaction by disconnecting one electrode from the power source. Allow all remaining bubbles to reach the surface. Record the level of the liquid in the buret, both the volume reading and the height of the meniscus above the surface of the liquid in the beaker. Also, record the temperature and barometric pressure in the laboratory.
19. Remove the metal electrode (do not disassemble the rest of the apparatus) and rinse it with 0.1 M  $\text{HC}_2\text{H}_3\text{O}_2$ . Use a paper towel to wipe off any remaining particles. Rinse with water and acetone. When dry, weigh it and record the mass to 0.001 g.
20. Return the electrode to the conducting solution, reconnect the electrode, and repeat steps 16 and 17. When you are finished, return the clean metal electrode to the supply bench and dispose of the conducting solution in the waste container. Be sure to empty the buret.

## RESULTS AND DISCUSSION:

You will need several data tables for your Results Section. For Part I, prepare a well-organized and labeled data table. Include all the data you collected in the lab and the predicted value of  $E^\circ_{\text{cell}}$  for the Cu-Zn cell that you calculated in the pre-lab assignment from the tabulated standard reduction potentials. For Part II, prepare a well-labeled data table that includes all of your data and also gives the identity of metals X and Y. To identify these metals, compare your experimentally measured values of  $E^\circ_{\text{cell}}$  to the predicted values that you calculated in the pre-lab assignment.

For Part III, prepare a table with the following information for each test: initial and final buret readings, the volume of gas generated, the height of the meniscus, initial and final electrode masses, the change in electrode mass, temperature, atmospheric pressure, vapor pressure of water at the measured temperature, the pressure exerted by dry  $\text{H}_2$ , the number of faradays passed, and the gram equivalent mass of the metal.

We will use the ideal gas law to determine the moles of  $\text{H}_2$  produced. In order to do so, we need to determine the pressure of the gas. The pressure inside the buret ( $P_{\text{inside}}$ ) is *less* than the pressure in the lab ( $P_{\text{atm}}$ ). There are two adjustments that must be made. First, we must correct for the difference in height between the meniscus and the surface of the water in the beaker. The pressure inside the beaker is given by (in kPa):

$$P_{\text{inside}} = P_{\text{atm}} - \rho hg$$

where  $\rho$  is the density of the solution,  $h$  is the height of the solution in the buret, and  $g$  is the acceleration due to gravity. You measured  $h$  during the experiment. We will assume the density of solution is equal to the density of water,  $1000.0 \text{ kg/m}^3$ . The acceleration due to gravity is  $9.81 \text{ m/s}^2$ . Note – you must use correct units (m) for height and you will need to find  $\rho hg$  in kPa.

The interior pressure is due to  $\text{H}_2$  gas alone. There is also water vapor in the gas phase. We will subtract this from  $P_{\text{inside}}$ . To find the vapor pressure of water, use the CRC Handbook of Chemistry and Physics,

available through the library. Calculate the pressure exerted by dry H<sub>2</sub> ( $P_{\text{H}_2}$ ) by subtracting the vapor pressure of water from  $P_{\text{inside}}$ .

$$P_{\text{H}_2} = P_{\text{inside}} - P_{\text{water}} = P_{\text{atm}} - \rho h g - P_{\text{water}}$$

Calculate the moles of H<sub>2</sub> produced using the ideal gas law. The number of faradays passed is equal to the number of moles of electrons used (see Introduction). Finally, the GEM of the metal can be found by dividing the number of grams of metal lost by the number of faradays passed.

Use the table provided in the introduction to identify your metal. Determine the charge,  $n$ , on the cations produced in the electrolysis using the following equation:

$$\text{Molar Mass} = \text{GEM} \times n$$

### QUESTIONS:

1. Explain how you identified unknowns X and Y. Discuss any uncertainty in your identifications.
2. What is the job of the salt bridge in a voltaic cell? Look this up in your textbook. Explain as completely as you can why a salt bridge is needed.
3. In Part III, we used a conducting solution in place of a salt bridge. This conducting solution functions in the same manner as a salt bridge. Write and balance the half reactions and the net cell reaction for this cell. Calculate the standard cell potential using the standard reduction potentials provided in your textbook.