

1. *Electrochemistry*

Introduction

A study of *electrochemistry* (Ebbing/Gammon, Chapter 20) generally consists of two principal topics. The first of these deals with the electricity obtained from spontaneous chemical reactions occurring in *voltaic cells*. The second concerns the application of electricity to drive chemical reactions within *electrolytic cells* in nonspontaneous directions.

Purpose

In this experiment you will study an electrolytic cell and several voltaic cells, including a concentration cell.

The design of electrochemical cells

A voltaic cell functions only when a complete electric circuit occurs. An external wire provides a path for electrons to travel from the anode to the cathode. The circuit is completed when the solutions surrounding these electrodes are in contact. Ions can then pass from one solution to the other. Because several different ways of achieving this contact have been devised, there are several designs for voltaic cells.

A salt bridge, a porous pot, a porous glass plug, or a membrane can be used to separate the solutions while maintaining electrical contact. These designs are shown in Figure 1.1. The voltaic cell that you encounter in this experiment will probably be one of these designs.

Electrolytic cells may differ from voltaic cells in one important respect. The solutions around the two electrodes do not always need to be separated. One solution may suffice. An example involving the electrolysis of water is shown in Figure 1.2.

Using a voltmeter

The voltmeter that you use in this experiment may be similar to one shown in Figure 1.1. Alternatively, it could be a pH meter operating as a voltmeter. Either of these instruments will enable you to measure the voltage from a voltaic cell. Moreover, either will allow you to identify the voltaic cell's anode and cathode.

You will find two terminals on your voltmeter. One of these (you will determine which one) must always be connected to the anode of any voltaic cell, and the other must always be connected to the cathode. The deflection of the voltmeter's needle will be positive only when the correct terminal is connected to the appropriate electrode. If the connections are reversed, a negative deflection will occur. You will use a zinc-copper voltaic cell (Figure 1.1; also Ebbing/Gammon, Section 20.2) to decide how the terminals must be connected. This information will enable you to identify the anode and cathode of any other voltaic cell.

FIGURE 1.1

A zinc-copper voltaic cell with (A) a salt bridge, (B) a porous pot, (C) a porous glass plug, and (D) a membrane. Both ions and water can pass through the membrane.

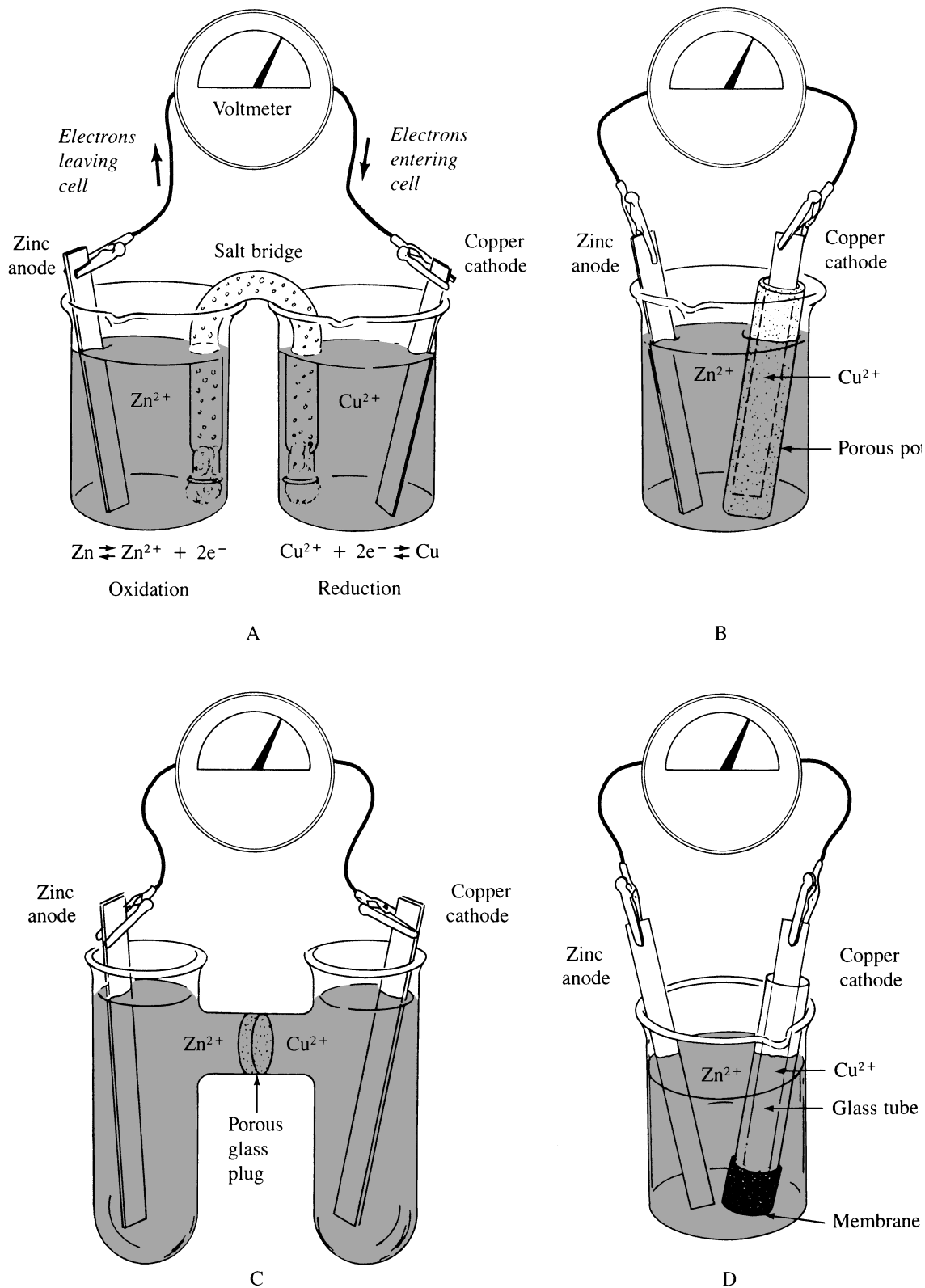
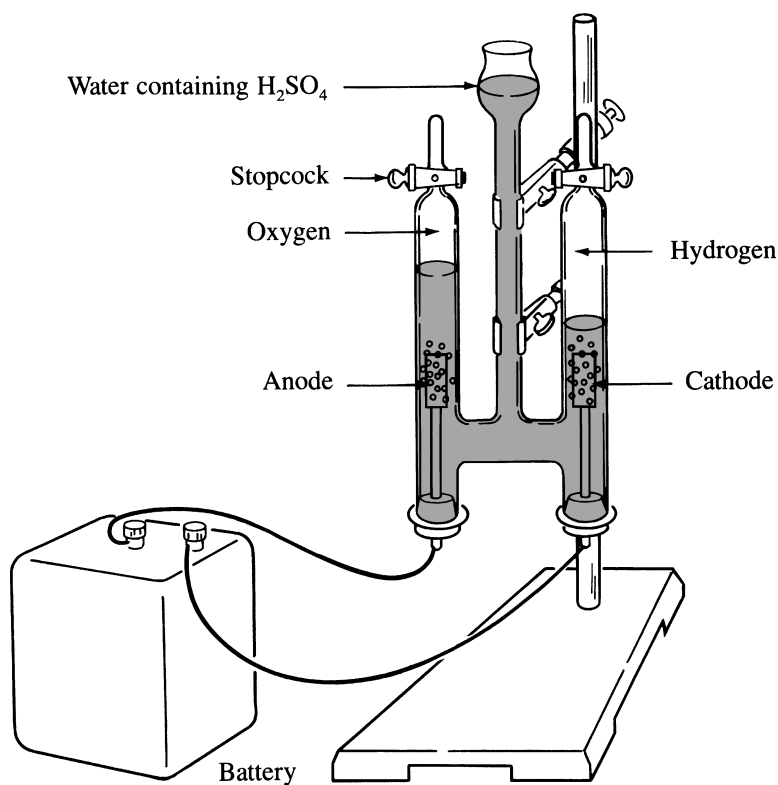


FIGURE 1.2
The electrolysis of water. Note that the electrodes are not separated by a porous barrier.

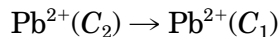


Concentration cells

A concentration cell is a voltaic cell in which the two half-reactions are identical but involve solutions at different concentrations. Take a lead concentration cell, for example. The half-reactions for this cell are

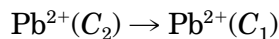


where C_1 and C_2 are the concentrations of Pb^{2+} ions around each electrode. The overall cell reaction is



If $C_1 = C_2$, the electromotive force (emf) of this cell will be exactly zero no matter what values C_1 and C_2 actually have. An emf will develop, however, when the concentrations of Pb^{2+} ions around the electrodes are different ($C_1 \neq C_2$). We can also say that the overall cell reaction will be spontaneous in the direction in which it is written when $C_2 > C_1$.

What makes this concentration cell work? It works because the process



is spontaneous whether it occurs inside or outside of a voltaic cell. The following example should help you understand the spontaneity of this process when it occurs outside of a voltaic cell. Suppose we have two solutions of Pb^{2+} ions

separated by a porous barrier. The concentrations of Pb^{2+} ions in these solutions will again be represented by C_1 and C_2 . If $C_2 > C_1$, the natural tendency is for ions to flow through the barrier in such a way that C_2 decreases and C_1 increases. Ions will continue to flow from one side of the barrier to the other until the concentrations of the solutions become equal. This process, which will occur without any outside intervention, is clearly spontaneous. As a result, it must also be spontaneous in the voltaic cell.

What emf will be delivered by a concentration cell? The emf can be calculated from the Nernst equation (Ebbing/Gammon, Section 20.7). At 25°C , this equation is

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q$$

where n is the number of electrons transferred in the overall cell reaction and Q is the reaction quotient. For the lead concentration cell we have

$$E_{\text{cell}}^{\circ} = 0.13 - 0.13 = 0.00 \text{ V}$$

$$Q = C_1/C_2$$

If $C_1 = 0.010 \text{ M}$ and $C_2 = 1.0 \text{ M}$, the emf will be

$$E_{\text{cell}} = - \frac{0.0592}{2} \log \frac{0.010}{1.0} = 0.059 \text{ V}$$

because $n = 2$ for the lead concentration cell. If, however, $C_1 = 0.00010 \text{ M}$ and $C_2 = 1.0 \text{ M}$ again, the emf will increase, so that its value is

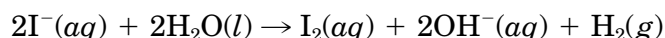
$$E_{\text{cell}} = - \frac{0.0592}{2} \log \frac{0.00010}{1.0} = 0.118 \text{ V}$$

These examples show that the emf of a concentration cell increases as the disparity between the concentrations of the two solutions increases.

Concept of the experiment

The experiment has four parts. When you have completed the entire experiment, you will have gained valuable insights into some of the fundamental aspects of electrochemistry.

In the first part, you will study electrolysis. A source of direct current, such as a 6-V battery, will provide the electricity. The electrolytic cell will consist of two graphite electrodes immersed in a solution of potassium iodide. The overall cell reaction will be



You will measure the pH of the solution before the electrolysis. After the electrolysis begins, you will be able to see the evolution of gas at one electrode and the appearance of a yellow-brown color at the other electrode. This color is due to aqueous iodine. After 15 min have elapsed, you will make a final pH

measurement, and from this you can determine the extent of this reaction and the average current that passed through the electrolytic cell.

In the second part, you will assemble a zinc-copper voltaic cell. You will determine the proper way to connect the voltmeter to the voltaic cell while you are measuring the cell's emf.

In the third part, you will determine the anodes, cathodes, and voltages of a series of voltaic cells. Each cell will have two of the following electrodes: $\text{Cu}^{2+}|\text{Cu}$, $\text{Fe}^{2+}|\text{Fe}$, $\text{Pb}^{2+}|\text{Pb}$, and $\text{Zn}^{2+}|\text{Zn}$ as well as Fe^{3+} , $\text{Fe}^{2+}|\text{Pt}$ (graphite may be used in place of platinum if necessary). You will be able to compare the emf from each cell with an emf that you will calculate from the data in Table 1.1.

Finally, you will examine a copper concentration cell. You will measure the emf and study the effect of altering the concentration of Cu^{2+} ions around one electrode.

Procedure

Getting started

1. Your laboratory instructor may ask you to work with one or two other students.
2. Obtain enough glassware and equipment to assemble a voltaic cell and an electrolytic cell.
3. Obtain a source of direct current.
4. If a salt bridge is required, ask your laboratory instructor about its composition.
5. Obtain the zinc, copper (2), lead, iron, graphite (2), and platinum (or graphite) electrodes and a voltmeter.
6. If your voltmeter is a pH meter, your laboratory instructor may want to give you some instructions in its use.
7. Locate a pH meter that can be used to measure pH. This instrument should be standardized at pH 10.0.
8. Obtain directions for discarding the solutions that you will use in this experiment.

Doing the electrolysis

1. Obtain 2.0 g of solid KI, using a platform balance, triple beam balance, or an electronic top-loading balance. Do not place this solid directly on the pan of the balance.
2. Transfer the solid to a clean 125-mL or 250-mL Erlenmeyer flask. Add 100 mL of distilled water from a graduated cylinder and swirl until a homogeneous solution is obtained.
3. Measure and record the pH of this solution. When you have an opportunity, calculate and record $[\text{OH}^-]$.
4. Place two graphite electrodes in a 150-mL beaker. Clamp the electrodes so that they cannot touch. Your laboratory instructor will tell you how to do this if it is not obvious from your equipment.

Table 1.1 Standard Electrode (Reduction) Potentials in Aqueous Solution at 25°C*

Cathode (Reduction) Half-Reaction	Standard Potential, E° (Volts)
$\text{Li}^+(aq) + e^- \rightleftharpoons \text{Li}(s)$	-3.04
$\text{K}^+(aq) + e^- \rightleftharpoons \text{K}(s)$	-2.92
$\text{Ca}^{2+}(aq) + 2e^- \rightleftharpoons \text{Ca}(s)$	-2.76
$\text{Na}^+(aq) + e^- \rightleftharpoons \text{Na}(s)$	-2.71
$\text{Mg}^{2+}(aq) + 2e^- \rightleftharpoons \text{Mg}(s)$	-2.38
$\text{Al}^{3+}(aq) + 3e^- \rightleftharpoons \text{Al}(s)$	-1.66
$2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq)$	-0.83
$\text{Zn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Zn}(s)$	-0.76
$\text{Cr}^{3+}(aq) + 3e^- \rightleftharpoons \text{Cr}(s)$	-0.74
$\text{Fe}^{2+}(aq) + 2e^- \rightleftharpoons \text{Fe}(s)$	-0.41
$\text{Cd}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cd}(s)$	-0.40
$\text{Ni}^{2+}(aq) + 2e^- \rightleftharpoons \text{Ni}(s)$	-0.23
$\text{Sn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Sn}(s)$	-0.14
$\text{Pb}^{2+}(aq) + 2e^- \rightleftharpoons \text{Pb}(s)$	-0.13
$\text{Fe}^{3+}(aq) + 3e^- \rightleftharpoons \text{Fe}(s)$	-0.04
$2\text{H}^+(aq) + 2e^- \rightleftharpoons \text{H}_2(g)$	0.00
$\text{Sn}^{4+}(aq) + 2e^- \rightleftharpoons \text{Sn}^{2+}(aq)$	0.15
$\text{Cu}^{2+}(aq) + e^- \rightleftharpoons \text{Cu}^+$	0.16
$\text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s)$	0.34
$\text{IO}^-(aq) + \text{H}_2\text{O} + 2e^- \rightleftharpoons \text{I}^-(aq) + 2\text{OH}^-(aq)$	0.49
$\text{I}_2(s) + 2e^- \rightleftharpoons 2\text{I}^-$	0.54
$\text{Fe}^{3+}(aq) + e^- \rightleftharpoons \text{Fe}^{2+}(aq)$	0.77
$\text{Hg}_2^{2+}(aq) + 2e^- \rightleftharpoons 2\text{Hg}(l)$	0.80
$\text{Ag}^+(aq) + e^- \rightleftharpoons \text{Ag}(s)$	0.80
$\text{Hg}^{2+}(aq) + 2e^- \rightleftharpoons \text{Hg}(l)$	0.85
$\text{ClO}^-(aq) + \text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{Cl}^-(aq) + 2\text{OH}^-(aq)$	0.90
$2\text{Hg}_2^{2+}(aq) + 2e^- \rightleftharpoons \text{Hg}_2^{2+}(aq)$	0.90
$\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightleftharpoons \text{NO}(g) + 2\text{H}_2\text{O}(l)$	0.96
$\text{Br}_2(l) + 2e^- \rightleftharpoons 2\text{Br}^-(aq)$	1.07
$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(l)$	1.23
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \rightleftharpoons 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)$	1.33
$\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-(aq)$	1.36
$\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- \rightleftharpoons \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$	1.49
$\text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) + 2e^- \rightleftharpoons 2\text{H}_2\text{O}(l)$	1.78
$\text{S}_2\text{O}_8^{2-}(aq) + 2e^- \rightleftharpoons 2\text{SO}_4^{2-}(aq)$	2.01
$\text{F}_2(g) + 2e^- \rightleftharpoons 2\text{F}^-(aq)$	2.87

* See Ebbing/Gammon Appendix I for a more extensive table.

5. Add 30 mL of the solution of KI to the beaker from a graduated cylinder.
6. Attach wires from the battery (or other source) to the electrodes. Immediately note and record the time.
7. Observe the solution for several minutes. What do you see? Record your observations.

- Allow the electrolysis to proceed for about 15 min. During this time, you can begin your studies of voltaic cells.
- After about 15 min have elapsed, disconnect the wires, noting the time to the nearest minute. Record the time.
- Remove the electrodes from the solution and examine them thoroughly. What do you see? Record your observations and the probable identity of any substance that may be present.
- Stir the solution thoroughly, and then measure the pH. When you have an opportunity, calculate and record $[\text{OH}^-]$.
- Calculate and record the change in $[\text{OH}^-]$ that occurred during the electrolysis.

Studying the zinc-copper voltaic cell

- Place 0.10 M $\text{Cu}(\text{NO}_3)_2$ in one compartment of a clean voltaic cell and 0.10 M $\text{Zn}(\text{NO}_3)_2$ in the other compartment.
- Clean the copper and zinc electrodes by dipping them briefly into about 40 mL of 6 M HNO_3 . Their surfaces will become bright and lustrous. Wash the electrodes with distilled water and dry them.

CAUTION: Handle the 6 M solution of nitric acid carefully. The acid can cause chemical burns in addition to ruining your clothes. If you get any of it on you, wash the contaminated area thoroughly and report the incident to your laboratory instructor. You may require further treatment.

- Insert the copper electrode in the solution of $\text{Cu}(\text{NO}_3)_2$, and insert the zinc electrode in the solution of $\text{Zn}(\text{NO}_3)_2$.
- Connect each electrode to a terminal on the voltmeter.
- If a negative deflection of the voltmeter's needle occurs, the connections should be reversed.
- Use a piece of marked tape to identify the terminal on the voltmeter that must be connected to the anode. Use another piece of marked tape to identify the terminal that must be connected to the cathode. You identified the anode and cathode of this cell in the Prelaboratory Assignment.
- Record the cell's emf.
- Disconnect the wires at the electrodes of the voltaic cell.

Studying the other voltaic cells

- You may begin this part of the experiment while the electrolysis is progressing. These studies can be interrupted when the electrolysis is completed.
- After you have read all of the instructions, determine the anodes, cathodes, and voltages of the following voltaic cells:
 - $\text{Cu}^{2+} | \text{Cu and Pb}^{2+} | \text{Pb}$
 - $\text{Cu}^{2+} | \text{Cu and Fe}^{2+} | \text{Fe}$
 - $\text{Cu}^{2+} | \text{Cu and Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$
 - $\text{Zn}^{2+} | \text{Zn and Pb}^{2+} | \text{Pb}$

- e. $\text{Zn}^{2+}|\text{Zn}$ and $\text{Fe}^{2+}|\text{Fe}$
- f. $\text{Zn}^{2+}|\text{Zn}$ and $\text{Fe}^{3+}, \text{Fe}^{2+}|\text{Pt}$
- g. $\text{Fe}^{2+}|\text{Fe}$ and $\text{Fe}^{3+}, \text{Fe}^{2+}|\text{Pt}$

If you are using a salt bridge, also include

- h. $\text{Pb}^{2+}|\text{Pb}$ and $\text{Fe}^{2+}|\text{Fe}$
- i. $\text{Pb}^{2+}|\text{Pb}$ and $\text{Fe}^{3+}, \text{Fe}^{2+}|\text{Pt}$

You should not study these two cells if you are using a porous pot, a porous glass plug, or a membrane, because the precipitation of PbSO_4 , which can occur at the junction of the solutions, would mar your results.

3. The solutions that are to be used for these voltaic cells are 0.10 *M* solutions of $\text{Zn}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, FeSO_4 (stored over iron wire or nails), and $\text{Cu}(\text{NO}_3)_2$, along with an iron solution composed of 0.050 *M* FeSO_4 and 0.050 *M* $\text{Fe}_2(\text{SO}_4)_3$ in 1 *M* H_2SO_4 .
4. Prepare the copper, iron, lead, and zinc electrodes by cleaning, rinsing, and drying them according to the directions given previously.

CAUTION: When you have completed this part of the experiment, wash your hands. Solutions containing lead are poisonous.

Studying a copper concentration cell

1. Add 1 mL of 0.10 *M* $\text{Cu}(\text{NO}_3)_2$ from a 5-mL or 10-mL graduated cylinder to a clean, dry 100-mL graduated cylinder. Add enough distilled water to bring the volume up to the 100-mL mark. Pour this solution into a clean beaker, and swirl or stir to obtain a homogeneous solution.
2. Clean the surfaces of two copper electrodes with 6 *M* HNO_3 . Wash the electrodes with distilled water and dry them.
3. Place an appropriate quantity of the diluted solution from Step 1 in one compartment of a voltaic cell and an appropriate quantity of 0.10 *M* $\text{Cu}(\text{NO}_3)_2$ in the other compartment.
4. Insert the copper electrodes into these solutions.
5. Use the voltmeter to identify the anode and cathode and to measure the emf. Record your results.
6. Add 10 drops of 0.10 *M* $\text{Cu}(\text{NO}_3)_2$ to the more dilute solution in the cell. Stir and repeat Step 5.
7. Remove the tape from the voltmeter when you are sure that you do not need to repeat any part of this experiment.

Electrochemistry

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Course: Team members:
Section:
Instructor:

Prelaboratory assignment

1. Provide definitions for the following terms:

a. Anode

b. Cathode

c. Voltaic cell

d. Electrolytic cell

e. Concentration cell

f. emf

2.
 - a. What is the overall cell reaction of the zinc-copper voltaic cell?

 - b. Identify the anode and cathode.

3.
 - a. What is the overall cell reaction in the electrolytic cell used in this experiment?

 - b. Identify the anode and cathode. Give the half-reactions that will occur at these electrodes.

4. Identify the half-cell reactions for the electrodes that you will study in the third part of this experiment.

5.
 - a. What is the overall cell reaction of a copper concentration cell?

 - b. Why is this a spontaneous reaction?

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- c. Identify the anode and the cathode. Use care in your answer because both electrodes are identical metals.

6. What safety precautions are cited in this experiment?

Electrochemistry

Date: Student name:
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Section:
Instructor:

Results

1. *Electrolysis*

Initial pH:

Initial $[\text{OH}^-]$: *M*

Time begun:

Observations:

Time ended:

Time elapsed:

Condition of electrodes after the electrolysis:

Final pH:

Final $[\text{OH}^-]$: *M*

$\Delta[\text{OH}^-]$: *M*

2. *Zinc-copper voltaic cell*

emf: V

3. *Other voltaic cells*

Electrodes	Emf (V)	Anode	Cathode
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4. *Copper concentration cell*

Anode:

Cathode:

emf: V

emf after 10 drops of 0.10 M $\text{Cu}(\text{NO}_3)_2$: V

- b. Use the Nernst equation, where necessary, to calculate E_{cell}° for each overall cell reaction. Include the zinc-copper voltaic cell.

3. Complete the following table, using your results from every voltaic cell, including the zinc-copper voltaic cell.

Overall Reaction in Voltaic Cell	Calculated E_{cell}° (V)	Expected E_{cell}° (V)*
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* From calculations using data in Table 1.1.

- b. Compare the calculated emf with the observed emf. Provide a tentative explanation of any major disagreement.
- c. How did the addition of 0.10 M $\text{Cu}(\text{NO}_3)_2$ affect the emf? Why?