

An Introduction to Electrochemistry

Objectives

The objectives of this laboratory are to:

- Understand what is meant by oxidation, reduction, voltaic cells, and electrolytic cells.
- Develop an electrochemical series based on potential differences between half-cells.
- Develop a working understanding of the Nernst equation.
- Investigate the chemical reactions occurring during the electrolysis of water.

Background

Electrochemistry is a branch of chemistry that affects you every day. Batteries which start your car, run calculators and wristwatches, and supply emergency power all operate on electrochemical principles. Corrosion of pipes, buildings, bridges, boats, cars, and planes can be prevented with knowledge of basic electrochemical principles. Nerve impulses are the result of electrochemical reactions in our body. Most general chemistry textbooks have a chapter on electrochemistry. It would be a good idea to review this chapter in your book before performing this laboratory.

Galvanic Cells and the Electrochemical Series

During Part I of this experiment, you will be building *galvanic cells* (also known as *voltaic cells*). Galvanic cells act as batteries, taking advantage of the fact that substances can spontaneously lose or gain electrons. The result of electrons being transferred between substances is electricity. One of the first commercial batteries, known as a Daniell cell, was developed in 1836. The Daniell cell looked similar to Figure 1, but used a copper rather than a lead electrode.

Although the figure may look complicated, it is really fairly simple. Each compartment, or side, of the galvanic cell is known as a *half-cell*. The metal strips in their respective solutions are known as *electrodes*. The ionic solution junction between the two half-cells is called a *salt bridge*. The galvanic cell makes use of the fact that different substances (in this case, zinc and lead) have different tendencies to gain and lose electrons. The lead electrode wants to gain electrons more than the zinc electrode does. Another way of stating this is that the zinc electrode wants to lose electrons more than the lead electrode. In this galvanic cell, the lead is *reduced*, or gains electrons and the zinc is *oxidized*, or loses electrons. Let's look at the concept of *oxidation* and *reduction* a bit more closely.

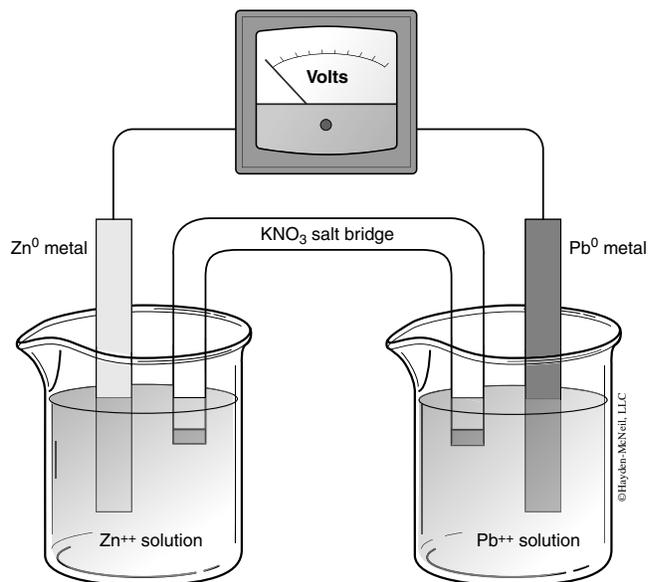
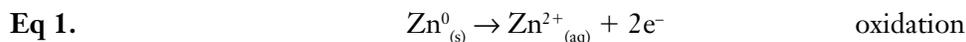
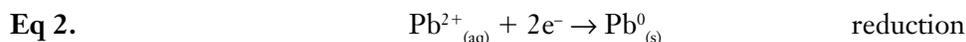


Figure 1. A zinc/lead galvanic cell.

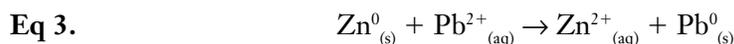
The zinc electrode is losing electrons, which are flowing to the lead electrode. Since the electrons are flowing away from the zinc electrode, the zinc is considered to be the negative pole and is known as the *anode*. The electrons are accepted at the lead electrode, making the lead the positive pole (known as the *cathode*). Since the zinc electrode is losing electrons, the zinc metal is becoming zinc ions and going into solution. This can be represented by the following equation:



The above reaction is called an *oxidation half reaction*. Conversely, in the other half-cell, the lead is gaining electrons, with lead coming out of solution to form lead metal. This is known as a *reduction half reaction* and can be represented by Equation 2:



Thus, the zinc electrode will eventually dissolve as it is converted to zinc ions, while the lead in solution will plate out as metallic lead onto the lead electrode. Equation 3, the combination of the two half reactions, results in the flow of electrons from the zinc electrode to the lead electrode ... a battery!



The *salt bridge* shown in Figure 1 allows electrical contact between the two solutions in the half-cells. The salt bridge also prevents mixing of electrode solutions and ensures electrically neutral solutions by providing a balancing flow of positive and negative ions.

The force pushing the electron away from the zinc electrode and the attractive force exerted on the electron as it approaches the lead electrode provide an excellent measure of the tendency for oxidation and reduction to take place in this reaction. In the case of zinc and lead, the sum of the forces moving the electron from the zinc to the lead is *theoretically* about 0.63 V. The exact voltage of such a cell depends upon the materials used for the electrodes, the concentration of the solutions, and the temperature. Your textbook discusses the theoretical prediction of cell voltages.

In Part I of this experiment, you will try other metal/ion half-cell combinations with the $\text{Pb}^0/\text{Pb}^{2+}_{(\text{aq})}$ half-cell. From this data, you will develop a table listing the various elements and ions in order of their tendency to gain or lose electrons.

The Nernst Equation

Theoretical predictions of tendency to gain electrons are used to predict the voltage difference between two electrodes. The voltage difference between electrodes, the cell voltage, is also called the *electromotive force*, or *emf* (E or E_{cell}). Under standard-state conditions (25°C, 1 M solution concentration, 1 atm pressure for gases), these theoretically predicted voltages are known as *standard emfs* (E° or E°_{cell}).

In reality, standard-state conditions are often difficult if not impossible to obtain. The *Nernst equation* allows cell voltages to be predicted when the conditions are not standard. Walter Nernst developed the following equation in the late 1800s while studying the thermodynamics of electrolyte solutions:

$$\text{Eq. 4} \quad E_{\text{cell}} = E^\circ_{\text{cell}} - (2.303 RT \log Q)/nF$$

In Equation 4, R is the gas constant (8.314 J mole⁻¹ K⁻¹), T is the temperature (Kelvins), F is Faraday's constant (96,485 coulombs/mole), n is the number of electrons transferred in the balanced oxidation/reduction reaction, and Q is the reaction quotient, or ([products]/[reactants]). This expression for Q is not completely general, and you will see it written a little differently in later courses. If the reactions are carried out at room temperature (25°C), the Nernst equation becomes

$$\text{Eq. 5} \quad E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591 \log Q)/n$$

Note: in Equations 4 and 5, if the reaction quotient is equal to 1, $E_{\text{cell}} = E^\circ_{\text{cell}}$.

In Part II of this experiment, you will measure voltages at various solution concentrations for the copper/zinc galvanic cell and compare your results with those calculated using the Nernst equation.

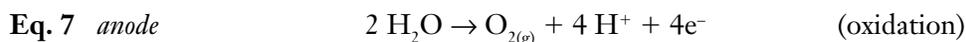
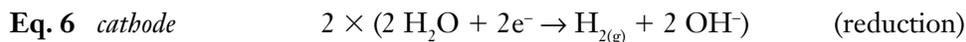
The Electrolysis of Water

Electrolytic cells can be thought of as being the opposite of galvanic cells. In an electrolytic cell, or *electrolysis cell*, electrical energy is used to force a chemical reaction to occur which, under normal conditions, would not occur spontaneously. Galvanic cells are often used to power electrolysis reactions. The process of electrolysis is very important in the

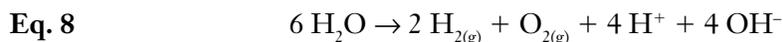
plating, purifying, and refining of metals. Perhaps the best known example of practical electrolysis is in the production of aluminum from its ore, bauxite. The production of aluminum via electrolysis is extremely energy intensive. The major cost savings in aluminum recycling is not in the metal saved, but in the electrical energy required to produce it from the ore.

In the not-so-distant future, oil will become an increasingly scarce commodity, amplifying the need to find replacements for gasoline (a portable fuel) to power cars, planes, and other means of transportation. Hydrogen is seen as a possible alternative to oil. Currently, the only big use of hydrogen as a fuel is in the rocket industry, where hydrogen fuels the main engines of the space shuttle. The large quantities of hydrogen needed for the space shuttle are produced from natural gas (which is also a depleting resource). However, the much larger quantities required to power a nation could only be produced practically by electrolysis. This, of course, would require a relatively cheap source of electricity, presumably solar or nuclear power. (It should be readily apparent from even this short paragraph that there are no easy answers to energy problems!)

To electrolyze water, the water must be more conductive than pure water (remember, the $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ of pure water are only $1 \times 10^{-7} \text{ M}$). To make water more conductive for electrolysis, a salt or acid is usually added. For this experiment, you will use a solution of 0.10 M KNO_3 to represent “conductive water.” A 9-volt battery will be used to provide the electrical power. Graphite electrodes attached to the battery leads will provide a nonreactive surface for the electrolysis reactions. According to Whitten et al., the following reactions will occur during the electrolysis of water:



The overall reaction (Equation 6 + Equation 7) is as follows:



giving the net reaction of



Thus, the net reaction of the electrolysis of water is hydrogen and oxygen gas. Hydrogen is produced at the cathode, with the solution becoming basic around that electrode. Oxygen is produced at the anode, with the solution becoming acidic around that electrode. The K^+ and NO_3^- from the potassium nitrate are much less readily reduced and oxidized than the H_2O and thus, take no part in the reaction. The KNO_3 serves only to conduct current through the solution.

In Part III of this experiment, you will observe the electrolysis of water and the acid/base properties of the solution around the electrodes.

Safety Precautions

Wear eye protection at all times and immediately clean up all spills!

Materials

Equipment

- MicroLAB Voltage Probe, wire leads with Cu wire probes, 9-volt battery with connecting wires and graphite (pencil lead) electrodes (check out from stockroom). *Do not let the battery wires or electrodes touch each other!*
- Plastic document protector, envelope containing metal pieces and sandpaper (supplied in lab)
- 50 mL beaker (from your locker)

Supplies

- Multi-EChem half-cell module

Reagents

- 0.10 M $\text{Pb}(\text{NO}_3)_2$, 0.10 M $\text{Ni}(\text{NO}_3)_2$, and 0.1 M KNO_3
- 0.00010 M, 0.0010 M, 0.010 M, 0.10 M, and 1.0 M $\text{Cu}(\text{NO}_3)_2$
- 0.10 M and 1.0 M $\text{Zn}(\text{NO}_3)_2$
- Yamada indicator

Experimental Procedures

Part I. Galvanic Cells and the Electrochemical Series

A simple and easy-to-use electrochemical cell can be built with the MicroLAB Multi-EChem Half-cell Module, illustrated in Figures 2 and 3.

This unit has eight small wells, each connected to a central salt bridge through a small channel. The salt bridge is made of an aqueous solution of potassium nitrate, and contacts the half-cells through a water-soaked porous cylinder. Ions can move through this porous barrier without allowing much mixing of the solutions. The center of the cylinder is filled with potassium nitrate to keep the cylinder wet and soaked with mobile ions.

Different metal/ion half-cell pairs can be set up in each of the outer wells, and the voltage produced by the two half-cells measured with a voltmeter as illustrated in Figures 2 and 3.

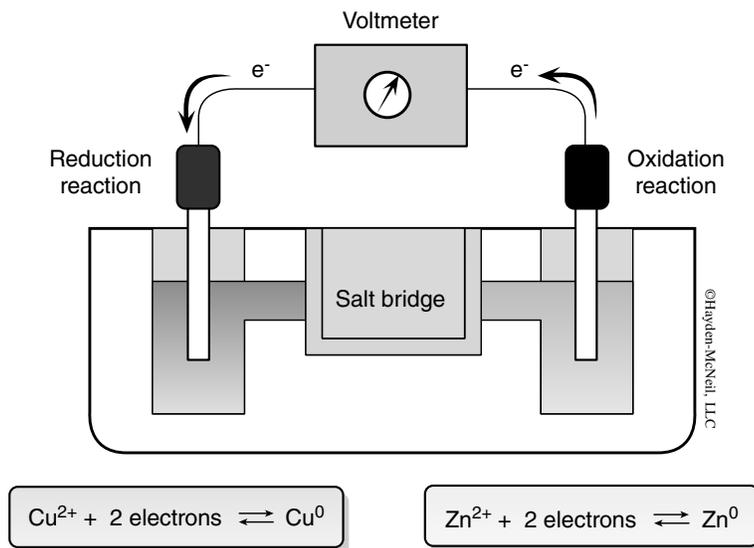


Figure 2. One can experimentally develop the electrochemical series by comparing a series of metal/ion pair half-cells against one “reference” metal/ion half-cell.



Figure 3. The Multi-EChem half-cell module can hold eight different metal/ion half-cells. If you use one as a reference, you can use the sign and magnitude of the voltage observed to order the elements in terms of their ability to gain or lose electrons, as compared to the reference metal/metal ion half-cell.

Set up your MicroLAB to measure voltage. Select the Voltage measurement, the dual banana jack voltage input, the ± 2.5 volt range, and accept the factory calibration.

Each of the wells will hold a different ion/metal half-cell. For example, in this figure, the left cell has a copper II nitrate solution and a copper wire.

You have black and red alligator clips connecting to the MicroLAB voltage input. If you get a positive voltage reading, electrons are running from the half-cell module into the black alligator lead, on to the MicroLAB voltmeter, and back out the red lead to the solution.

In this example (Figures 2 and 3), the voltage reads positive, indicating that the zinc/zinc ion half-cell on the right is producing electrons. The reaction (see Figure 2) is going to the left. It is an **oxidation** reaction. $\text{Zn}^{2+} \rightleftharpoons 2 \text{ electrons} \leftarrow \text{Zn}^0$. The copper/copper ion half-cell on the left in Figures 2 and 3 is accepting electrons. It is a **reduction** reaction. This reaction is going to the right: $\text{Cu}^{2+} \rightleftharpoons 2 \text{ electrons} \rightarrow \text{Cu}^0$.

By convention, oxidation–reduction reactions are always written from left to right as reduction reactions. A longer arrow can be used to indicate the predominant direction of the reaction.

Half-Cells and Ion Path

The lower channel from each half-cell well to the central salt bridge area provides a non-drying, low resistance aqueous path for ions up to the porous salt bridge membrane. The porous membrane is conditioned before use by soaking the unit with KNO_3 solution. This fills the pores in the membrane and prevents solutions from leaking from one half-cell to another. The aqueous salt bridge inside the circular porous membrane contacts all half-cells equally.

Half-Cell Overflow Volume

The milled overflow volume above each channel to the salt bridge is there to catch overflow as you fill the half-cell well. It prevents cross-contamination of half-cell solutions during filling. If you use a plastic pipette to deliver the ion solution to the well, it is easy to stop filling when the lower channel is full.

Experimental Development of the Electrochemical Series

Starting with the Pb/Cu combination, measure the voltages produced by the filter paper galvanic cells. Using the voltage probe, touch the copper wires to the metal strips on either side of the same filter paper, as shown in Figure 2. *Do not allow the probes or alligator clips to come in contact with the solutions.* Position the probes so that you read a positive voltage for the Pb/Cu system and note which color probe is on the Pb. The readings may fluctuate somewhat; if so, select an average value to record. You must press hard on the copper wire probes to get a good contact with the metal pieces.

Measure the voltages from the Pb/Zn system and the Pb/Ni system, **always using the same color probe on the Pb as you did for the Pb/Cu combination.** Record these voltages on the **Data Summary sheet** at the end of this chapter. Make sure you indicate the relative position of the reduction reactions you observed with respect to the lead half reaction. Your table may resemble the following, with the reaction for your most positive voltage at the top, and the reaction for your least positive (or most negative) voltage on the bottom.

Example electrochemical series table

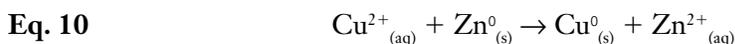
Reaction	Cell Voltage Compared to Pb ⁰ /Pb ²⁺ Half-cell
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0$?
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}^0$?
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}^0$	0.00 mV
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}^0$?

Note: This is not necessarily the order you will have; this is simply an example.

According to your table, which half-cell reaction has the greatest tendency toward reduction; that is, to gain electrons? Which half-cell has the greatest tendency toward oxidation? Based on your electrochemical series table, what would you predict for the voltage of a copper/zinc cell? *Build* a copper/zinc cell and measure the voltage. How does this compare with your prediction?

Part II. The Nernst Equation

In this part of the experiment, you will be examining the effect of solution concentrations on the cell voltage for the reaction



The Nernst equation allows you to calculate E_{cell} as a function of the concentrations of reactant and product. For the above reaction at 25°C, the Nernst equation can be rewritten as Equation 11.

Eq. 11
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0591 \log ([\text{Zn}^{2+}] / [\text{Cu}^{2+}]))/2$$

Remember, solids and pure liquids are not included in the Q expression. Theoretically, E°_{cell} for the above reaction is 1.10 V. Thus, a value for E_{cell} can be calculated, knowing $[\text{Zn}^{2+}]$ and $[\text{Cu}^{2+}]$.

Set up five zinc/copper cells using the following Zn^{2+} and Cu^{2+} solution concentrations. The cells will look like the one shown in Figure 2, except you'll use copper instead of lead.

Cell #	[Cu ²⁺]	[Zn ²⁺]
1	1.0	1.0
2	0.10	1.0
3	0.010	1.0
4	0.0010	1.0
5	0.00010	1.0

Measure the voltage (E_{cell}) from each of the above half-cell combinations. Record this voltage on the Data Summary sheet at the end of this experiment. Assuming $E_{\text{cell}}^{\circ} = 1.10$ V and the temperature of the room you are working in is 25°C , calculate E_{cell} for each of the above half-cell combinations. Record this calculated voltage on the data sheet.

How do your measured and calculated values for E_{cell} compare? If they differ significantly, can you offer any explanation for the differences? Pay attention to the units you are comparing.

Part III. The Electrolysis of Water

You will build an electrolytic cell using a 9-volt battery attached to two graphite (pencil lead) electrodes. *Do not let the battery wires or electrodes touch each other.* Place several mL of 0.1 M KNO_3 in a 50 mL beaker, and add about 8 drops of Yamada indicator. Then, place the graphite electrodes, connected to the battery, in the solution. *Do not allow the alligator clips to touch the solutions; only the graphite electrodes should touch the solution.* Figure 4 shows the properly configured cell for the electrolysis of water.

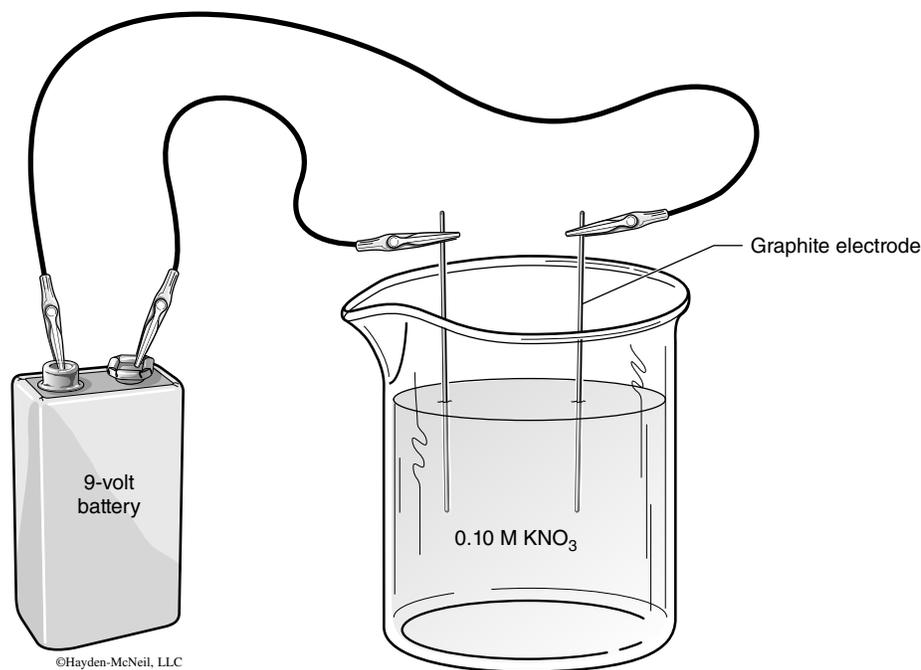


Figure 4. Cell configuration for the electrolysis of water.

You will observe gas being evolved at each electrode. You will also notice that the color of the Yamada indicator is different around each electrode. In acid solution, Yamada gives an orange-to-red color; in base, the color is purple or blue. Based on the relative amount of gas being produced at each electrode and the color of the Yamada around each electrode, which electrode is the anode and which electrode is the cathode? (Hint: Your observations should support the half reaction which you believe is occurring at each electrode. Refer to Equations 6 and 7.)

Note: Parts IV and V do not require any additional laboratory measurements. These parts use data you have already obtained and simply require additional calculations.

Part IV. Comparison of Calculated and Measured EMFs

Using a table of standard reduction potentials (e.g., from your textbook) and the Nernst equation, calculate E_{cell} for the three galvanic cells you built in Part I. Compare your calculated values of E_{cell} with those measured in Part I. If the values are significantly different, can you offer an explanation for why they are different?

Note: E° for Fe^{3+}/Fe is -0.036 V .

Part V. More Exercises Using the Nernst Equation

With the values you calculated in Part II, use the spreadsheet to make a plot of E_{cell} (calc) versus $\log([\text{Zn}^{2+}]/[\text{Cu}^{2+}])$. Graph a linear regression plot for the data. Include a copy of this graph with your report. What is the slope of this line? What does the slope of the line represent (Equation 11)? What should the slope of the line be equal to? What is your value for the y-intercept? What is the significance of the y intercept; that is, what does the y-intercept represent? What should the y-intercept be equal to?

Pre-Lab Questions

Make sure you can answer these before you enter the lab!

- Given the following half-cell reactions occurring in a galvanic cell:



- Which half reaction is the *oxidation* half reaction?
 - Which half reaction is the *reduction* half reaction?
 - Write the overall reaction which results from the two half reactions above.
- What is the function of the *salt bridge* in a galvanic cell?
 - Using your answer from 1c and the Nernst equation, calculate the E_{cell} at 25°C if $[\text{Zn}^{2+}] = 0.10\text{ M}$ and $[\text{Cu}^{2+}] = 1.0\text{ M}$. The E°_{cell} for the correct overall reaction in 1c is 1.10 V .

CHAPTER

10

Worksheet

<i>Name</i>	<i>ID No.</i>
<i>Instructor</i>	<i>Course/Section</i>
<i>Partner's Name (if applicable)</i>	<i>Date (of Lab Meeting)</i>

Data Summary**Part I. Galvanic Cells and the Electrochemical Series**

Cell Combination	Cell Voltage
Pb/Zn	
Pb/Cu	
Pb/Ni	
Pb/Pb	

Cell Combination	Cell Voltage Prediction	Cell Voltage Experimental
Cu/Zn		

How well did your prediction match the experimental value?

If not, what is a possible explanation?

Electrochemical Series Table

Reaction	Cell Voltage Compared to Pb ²⁺ /Pb ⁰ Half-cell

Part II. The Nernst Equation

[Cu ²⁺]	[Zn ²⁺]	[Zn ²⁺]/[Cu ²⁺]	log{[Zn ²⁺]/[Cu ²⁺]}	E _{cell} (meas)	E _{cell} (calc)
1.01	1.0				
0.10	1.0				
0.010	1.0				
0.0010	1.0				
0.00010	1.0				