

Electrochemistry and Concentration Effects on Electrode Potentials

Special mention and thanks goes to Dr. Timothy Friebe for his help in developing this laboratory write-up.

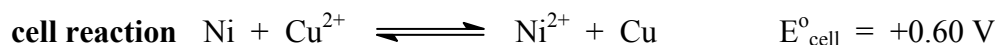
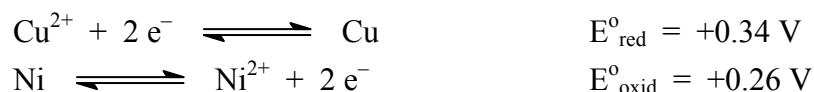
Introduction

You have already studied oxidation-reduction reactions in the previous laboratory experiment. This means you already have an understanding of half-reactions and how they contribute to the overall redox reaction. In those experiments, the oxidizing and reducing agents were in the same container. In this experiment, you will see that oxidation-reduction reactions can occur between the reactants in separate containers. This can happen when electrons are transferred between the reactants through a wire that connects the two containers.

Before the topic of the electrochemical cell can be introduced, there are a few terms that you must be familiar with. One of the most important terms is standard reduction potential (E°_{red}). This value is for the half-reaction which represents the reduction of a metal. Table I located at the end of the procedure for this experiment has some of the standard reduction potentials you will use in this experiment. The standard reduction potential is a quantitative measure of a substance's tendency to accept electrons under standard conditions (1 atm of gases and 1 M concentration) and is measured in volts. The more positive the reduction potential, the greater the tendency for reduction to occur. For the half-reaction that represents the oxidation of a metal, you can determine the standard oxidation potential (E°_{oxid}) for the half-reaction. This value has the same numerical value as the standard reduction potential but the opposite sign. For example, aluminum ion has a standard reduction potential value of -1.65 V (in going to aluminum metal). This means the standard oxidation potential for aluminum metal is $+1.65 \text{ V}$. The standard cell potential (E°_{cell}) is the sum of the standard oxidation and reduction potentials.

To explain how an electrochemical cell works, an example will be provided as well as how to calculate a standard net potential and compare it to your experimental or net cell potential value. If you were to construct a nickel-copper electrochemical cell, you would start off by placing a strip of nickel into a nickel(II) salt solution. It should be pointed out to you that all of the solutions are aqueous. You would then place a strip of copper into a copper(II) salt solution. The next step is to connect one end of a wire to the nickel strip and the other end to the copper strip. Electrons will pass through this wire between the nickel and the copper strip. If you wanted to predict which direction the electrons would flow through the wire, you can look up the standard reduction potentials for nickel and copper. The E°_{red} value for nickel ion is -0.26 V and $+0.34 \text{ V}$ for copper ion. This means that the Cu^{2+} ion has a greater tendency to accept electrons than the Ni^{2+} ion. Therefore, the electrons will pass through the wire from the nickel strip to the copper strip. However, this can only happen if a second connection is provided to complete the electrical circuit. This second connection is called a salt bridge and is placed in both solutions of the two containers. You now have an electrochemical cell. The electrochemical cell is a system that utilizes a spontaneous oxidation-reduction reaction to pump electrons through an electrical circuit. This system is composed of two parts or half-cells. In this example there is the nickel half-cell where nickel is being oxidized and the copper half-cell where the copper(II) ion is being reduced. The metal strips are called electrodes. The electrode in the half-cell where oxidation

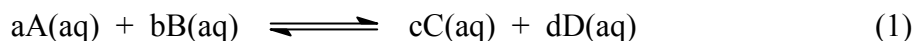
occurs is called the anode and the electrode in the half-cell where reduction occurs is called the cathode. The cell potential can be measured by connecting a voltmeter between the half-cells. This is what you will do and you can use Figure 1 as a reference to check your set up as well as asking your instructor. If you wanted to approximate what your observed voltage should be for this oxidation-reduction reaction, you can simply add the two half-reactions together and calculate the standard net potential. Since copper half-cell is undergoing reduction, the half-reaction will be represented as a reduction and the nickel half-cell will have the half-reaction represented as an oxidation.



The reading on your voltmeter may not be exactly +0.60 V. You are not working under standard conditions, but the important thing is that the ratio of the concentrations is 1:1. Therefore, you would still measure the standard cell potential. Any differences in the readings would come from other sources such as resistance in the salt bridge, lack of calibration of the voltmeter and the concentrations of the two cells not being exactly the same, for whatever reason.

In the second half of this experiment is the quantitative effect concentration changes have on cell voltage.

The quantitative effects are given by the Nernst equation. For example, the redox reaction:



is described by the Nernst equation:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \qquad (2)$$

where E°_{cell} is the voltage that can be calculated from the standard reduction potentials of the half-reaction components in the electrochemical cell. The symbol **n** represents the total number of electrons being transferred in the **balanced** cell reaction. So, if you recall from the introduction in the previous laboratory, the reaction between nickel and copper had two electrons transferred in the reaction. This means that n would be two. Looking at this equation, you see that increasing the concentration of the products lowers the voltage of the cell since the log term will be larger making the value of E_{cell} smaller.

Equation (2) represents the Nernst equation for the entire cell. When determining how the concentration of the silver ion affects the total cell potential, you must first determine how the concentration of the silver ion affects the half-cell reduction potential. The reaction for the half-cell reduction occurring in today's experiment is:



The analogous Nernst equation for reaction (3) is:

$$E = E^\circ - \frac{0.0591}{1} \log \frac{1}{[\text{Ag}^+]} \quad (4)$$

The electrochemical cell you are working with will also be made up of two half-cells but in this case one is a saturated calomel electrode while the other is a silver metal electrode. The cell potential is the sum of the two electrode potentials; one potential contributed by the calomel electrode and one contributed by the silver/silver ion electrode. You will take three different solutions with a different concentration of silver ion and measure the cell potential by placing both the calomel electrode and the silver electrode into each solution. This will give you three different potential values (E_{cell}). You are then going to find your average **standard reduction potential** value (E°) for the half-reaction using equation (4). You will know the concentration of the silver ion and the value of n . You must first determine E for the silver ion reduction by using the value that you read off of the potentiometer and the value of the standard reduction potential for the calomel electrode. The easiest way to do this is to think of a number line with both positive and negative numbers. For example, let's say you read +0.987 V off of the potentiometer when you place the electrodes in the 0.010 M silver ion solution. The value +0.987 V is the distance on the number line (and the direction) between the half-cell potential of the calomel electrode and the half-cell potential of the silver electrode. The standard reduction potential of the calomel electrode is +0.243 V. If the difference between the potential values for the calomel electrode and the silver electrode is +0.987 V (the positive sign means to the right of the calomel electrode on the number line), then the reduction potential value for the silver electrode (E) is +1.230 V (0.243 + 0.987). Using equation (4), you find your standard reduction potential (E°) for silver to be 1.348 V. This is just an example, your numbers most likely will not be near the value in this example. It should be noted that when you have a negative cell potential reading, the difference is now to the left of the calomel electrode on the number line. If for example your reading on the potentiometer is -0.439 V. This would mean that the potential value of the silver electrode in this case is -0.196 V (-0.439 + 0.243).

The third part of this experiment has you making a saturated AgCl solution in 0.100 M Cl^- . You will determine the concentration of the silver ion in this solution using **your** average E° value and your measured E (with respect to calomel) with equation (4) and the K_{sp} of AgCl.

Procedure

Part I:

Construct a salt-bridge by **completely** filling a U-tube with 0.5 M KNO_3 solution and plugging both ends with a cotton ball. Make sure the solution stays in when the tube is inverted and that the cotton balls are soaked with the KNO_3 solution.

Place about 25 mL each of 0.10 M zinc(II) sulfate solution, 0.10 M copper(II) sulfate solution, and 0.10 M iron(II) ammonium sulfate solution in 3 **separate** 50-mL beakers. Label the beakers '**zinc**', '**copper**', and '**iron**'. Clean strips of zinc and copper and an iron nail with steel wool.

Constructing a Zinc–Copper Electrochemical Cell

Referring to Figure 1, alligator clip the copper strip to one voltmeter terminal and alligator clip the zinc strip to the other voltmeter terminal. Dip the copper strip in the beaker containing the copper solution and the zinc strip in the beaker containing the zinc solution **at the same time**. Invert the salt-bridge into **both** beakers. Note the voltage and remove the salt-bridge immediately. If you have a negative reading on your voltmeter, reverse the connections to the metal strips and dip salt-bridge again. The metal attached to the black lead is the anode. Record the voltage **and** identify the anode and cathode of the cell.

Constructing an Iron–Copper Electrochemical Cell

Rinse both ends of the salt-bridge with a little 0.5 M KNO_3 solution. Connect the iron nail to one terminal of the voltmeter as before. Keep the copper strip from Part I attached to the other lead. Dip the metal strips into the proper solution and connect them with the salt-bridge as before. Record a positive reading and identify the anode and cathode.

Constructing an Iron–Zinc Electrochemical Cell

Rinse the ends of the salt-bridge. Keeping the iron nail attached to the voltmeter, replace the copper strip from above with the zinc strip. Dip the metal strips into the corresponding solution and connect them with the salt-bridge as before. Record a positive reading and identify the anode and cathode.

Part II

Be aware that Ag^+ solutions will stain your skin for several days, so handle the following solutions with care.

1. Place **about** 25 mL of 0.0010 M Ag^+ solution of in a 50-mL beaker.
2. Attach a calomel electrode to the black lead on the voltmeter and carefully rinse the salt bridge at the tip. Attach a clean (steel wool) strip of silver metal to the red wire of the voltmeter. Dip both electrodes into the Ag^+ solution, taking care not to have the two electrodes touch. Take the reading 3–5 seconds after placing the electrodes in the solution. The cell potential of the first solution should be between 0.3 and 0.5 V. If it is not see the instructor; you might need to get a new calomel electrode. Rinse the electrodes after reading the cell voltage and repeat this procedure with 0.010 M Ag^+ and 0.10 M Ag^+ . The reading should increase, but not go above 0.8 V.

Part III

1. Prepare a saturated AgCl solution by adding one drop of 0.10 M Ag⁺ to 25 mL of 0.10 M HCl. Insert the electrodes into this solution and measure the potential as before.

Questions

1. a. Calculate the **standard** cell potential of a cell constructed from Mg²⁺/Mg and Ni²⁺/Ni (Table I). Which is the anode and which is the cathode?
b. Using the Nernst Equation, what would be the potential of a cell with [Ni²⁺] = [Mg²⁺] = 0.10 M?

Data Treatment and Discussion

1. For **each electrochemical cell**, calculate the standard cell potential in the same manner shown in the introduction section of this laboratory experiment. Include the half-reactions and electrode potential values. Compare the calculated cell potentials to the measured voltages of your electrochemical cells. Describe the possible sources of error.
2. Using your data from the first three Ag/Ag⁺ cell potential readings, determine the **average** standard reduction potential (E^o) for silver ion.
3. Use your average value of E^o to determine [Ag⁺] in the fourth solution.
4. Knowing that [Cl⁻] is 0.10 M in the fourth cell, calculate K_{sp} of AgCl. Compare with a **published** value of K_{sp} (give the reference). Describe any source of error.

Conclusion

List the cell voltages, average E^o of Ag/Ag⁺, the [Ag⁺] in saturated AgCl, and your K_{sp} of AgCl.

Figure 1. Diagram of an Electrochemical Cell

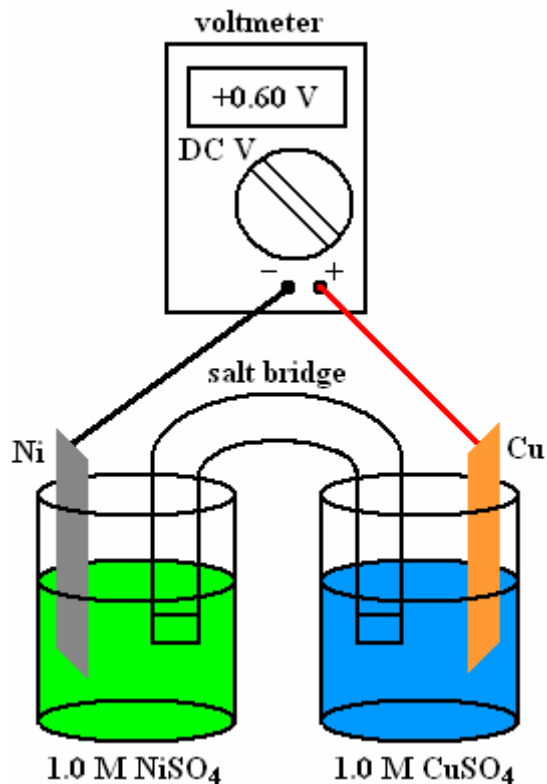


Table I. Standard Reduction Potentials for Selected Metals

<u>Half-Reaction</u>	<u>E^o_{red}(V)</u>
Mg ²⁺ + 2 e ⁻ ⇌ Mg	-2.37
Al ³⁺ + 3 e ⁻ ⇌ Al	-1.65
Zn ²⁺ + 2 e ⁻ ⇌ Zn	-0.76
Fe ²⁺ + 2 e ⁻ ⇌ Fe	-0.44
Ni ²⁺ + 2 e ⁻ ⇌ Ni	-0.26
Cu ²⁺ + 2 e ⁻ ⇌ Cu	+0.34
Ag ⁺ + e ⁻ ⇌ Ag	+0.80