

Electrochemical Cells and the Nernst Equation

Objective: To observe the effect of concentration on electrochemical potential; to use these results to verify the Nernst equation

Materials: 1.0 M copper(II) nitration solution, $\text{Cu}(\text{NO}_3)_2$; 1.0 M zinc nitrate solution, $\text{Zn}(\text{NO}_3)_2$; saturated solution of potassium nitrate, KNO_3 (for salt bridge); strips of copper metal and zinc metal (electrodes)

Equipment: Two 50-mL beakers; filter paper (cut in strips for salt bridge); 50-mL volumetric flask; voltmeter with leads/clips; 10-mL pipet; pipet bulb

Safety: Salt solutions can be irritants; wear safety goggles at all times in the lab.

Waste Disposal: Used filter paper (salt bridge) can be discarded in the waste basket.

INTRODUCTION

Electrochemistry is the study of chemical reactions and processes that involve the transfer of electrons. There are numerous practical applications of such reactions, including electroplating, corrosion protection, and the industrial production of materials such as aluminum and sodium hydroxide.

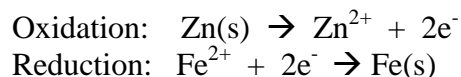
One of the more common applications is the construction of **batteries**, or devices that take advantage of the spontaneous electrochemical reactions to generate electricity. These reactions take place in an electrochemical cell that may contain the reactants dissolved in solution (a “wet-cell” battery) or suspended in a solid or semi-solid matrix (a dry cell). The cell is constructed so that the spontaneous movement of electrons must follow a certain path, and the resulting electric current can be used to do work (e.g., power a flashlight, lap-top computer, or cell phone).

The spontaneous transfer of electrons between reactants is related to the ability of the substances to gain or lose electrons. Consider the reaction in Equation (1).



We can describe the overall reaction in terms of the transfer of electrons. We define **oxidation** as a loss of electrons, and **reduction** as a gain of electrons. In this reaction, the Zn(s) on the left *loses* 2 electrons, or is oxidized. The Fe^{2+} ion in solution *gains* 2 electrons, or is reduced. Since the overall reaction involves both an oxidation and a reduction, we call it a **redox** reaction.

We can take the overall reaction and look at each of the processes separately:



The net reaction is the sum of these two **half-reactions**. Whether or not the net reaction proceeds spontaneously depends on the relative tendency of the species involved to gain or lose electrons. This tendency can be quantified by a **standard reduction potential (E°)**, which reflects the tendency of a substance to be reduced under standard conditions (e.g., one atm of pressure and/or 1.0 M concentration). Values for standard reduction potentials for many half reactions can be found in your textbook. The more positive the value for E° , the greater the tendency of the species involved to be reduced. The more negative the value of E° , the less the tendency of the species to be reduced (or, conversely, the greater its tendency to be oxidized).

The net reaction in Eq. (1) proceeds spontaneously. If we place a strip of Zn metal in contact with a solution of Fe^{2+} ions, electrons will be transferred directly between the Zn metal and the Fe^{2+} ions, and we cannot use these electrons to do work. If we isolate the half reactions into separate cells, we can construct a device where the movement of electrons is controlled and can be harnessed to do work. Such a device is called an **electrochemical cell**.

A typical electrochemical cell is illustrated in Figure 1. If the cell utilizes a spontaneous redox reaction to generate electricity, it is called a **galvanic cell**. Batteries are examples of galvanic cells. If we supply electricity to drive a non-spontaneous reaction, then the cell is called an **electrolytic cell**. Electroplating is typically performed in electrolytic cells.

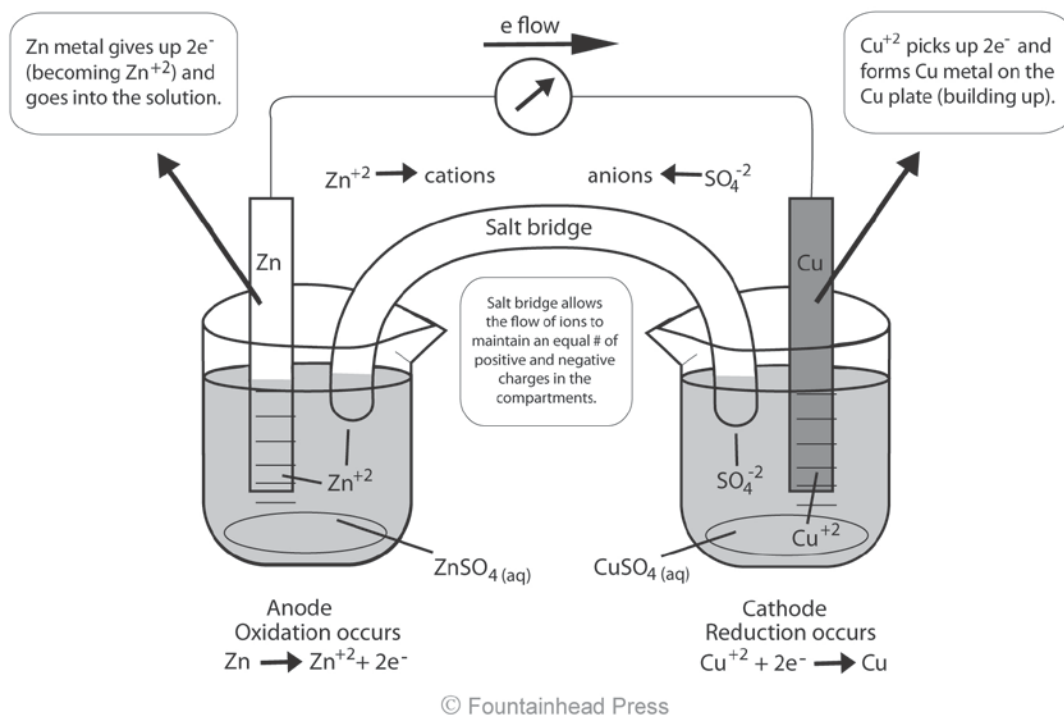
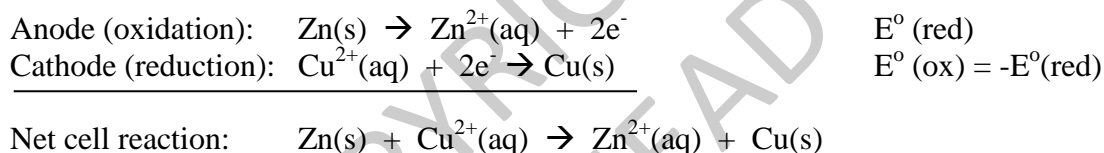


Figure 1. Typical galvanic electrochemical cell.

The cell illustrated in Figure 1 contains many components common to electrochemical cells. First, the reaction is divided between two **half-cells**; each half cell contains a solid **electrode**, which provides a surfaced for the exchange of electrons. The electrode where oxidation occurs is called the **anode**, while reduction occurs at the **cathode**. Since the two half reactions are separated, electrons must flow through a wire that extends from the anode to the cathode. In Figure 1, the wire is connected to a **voltmeter**, which is a device that can measure the driving force behind the flow of electrons. This driving force, sometimes called the “electromotive force” (or emf) has units of volts. The voltmeter could be replaced with a light bulb or other device, and the flow of electrons between anode and cathode could be used to power the device.

The **salt bridge** in the figure is needed to maintain a closed circuit and to prevent accumulation of charge in the half cells. It can be a gel-filled tube or a piece of paper containing dissolved salt. As electrons are lost from the anodic half-cell, the negative charges are replaced by the migration of anions from the salt bridge to the anodic solution. As electrons arrive at the cathode they react with cations in solution to form solid metal. Cations from the salt bridge migrate into the cathode solution to replace cations that are reduced at the cathode.

In this lab exercise you will construct two different electrochemical cells. The first is known as a Daniell cell. The half reactions and net cell reaction for the Daniell cell are:



The overall cell potential under standard conditions can be calculated as

$$E^{\circ}_{\text{cell}} = E^{\circ}(\text{red}) + E^{\circ}(\text{ox}) = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode})$$

where $E^{\circ}(\text{cathode})$ and $E^{\circ}(\text{anode})$ are the standard reduction potentials for these half-cell reactions. A spontaneous net cell reaction (e.g, a galvanic cell) would yield a positive value of E°_{cell} .

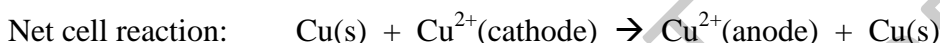
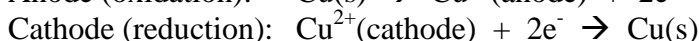
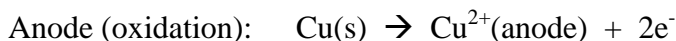
But what if the cell concentrations are not at standard states of 1.0 M concentrations? We can determine the cell potential under non-standard conditions by adding a term that corrects for deviations from standard states. The equation that relates E_{cell} to E°_{cell} and the non-standard cell conditions is called the **Nernst equation**:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q \qquad (2)$$

where R is the universal gas constant in appropriate units (8.314 J/mol·K), T is absolute temperature (in K), F is Faraday’s constant (96486 coul/mol e⁻), n is the number of electrons transferred in the net cell reaction, and Q is the reaction quotient. For the net reaction in the Daniell cell, this is the expression for $Q = [\text{Zn}^{2+}] / [\text{Cu}^{2+}]$.

If we examine Eq. (2) and the net cell reaction we can see how changes in concentration will affect the cell potential. If all species are at standard states (1.0 M concentrations), then the value of Q is unity and $E_{\text{cell}} = E^{\circ}_{\text{cell}}$. If the reaction is spontaneous, E_{cell} will be positive. What happens if the concentration of Cu^{2+} decreases? According to Le Chatelier's Principle, we would expect the cell reaction to shift left (i.e., become less spontaneous in the forward direction), which would result in a decrease in the value of E_{cell} . Decreasing the $[\text{Cu}^{2+}]$ would *increase* the value of Q , which according to Eq. (2), would decrease E_{cell} .

The second cell investigated in this lab is called a **concentration cell**. It uses the same half-reaction in both the anodic and cathodic half-cells, but at different concentrations. Consider the following half-cell and net cell reactions:



The expression for the reaction quotient is $Q = [\text{Cu}^{2+}]_{\text{anode}} / [\text{Cu}^{2+}]_{\text{cathode}}$. Since the half reaction in both half cells involves the same species, the E° for the anode and cathode are equal, and $E^{\circ}_{\text{cell}} = 0$. Now, the Nernst equation reduces to:

$$E_{\text{cell}} = -\frac{RT}{nF} \ln \left(\frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}} \right) \quad (3)$$

When the Cu^{2+} ion concentrations in each cell are the same, $Q = 1$ and $E_{\text{cell}} = 0$. When $[\text{Cu}^{2+}]_{\text{anode}} > [\text{Cu}^{2+}]_{\text{cathode}}$, then $Q > 1$, and $E_{\text{cell}} =$ negative (not spontaneous). Conversely, when $[\text{Cu}^{2+}]_{\text{anode}} < [\text{Cu}^{2+}]_{\text{cathode}}$, then $Q < 1$ and $E_{\text{cell}} =$ positive. Electrons will flow spontaneously from the anode to the cathode. The $[\text{Cu}^{2+}]_{\text{anode}}$ will increase and $[\text{Cu}^{2+}]_{\text{cathode}}$ will decrease until they are equal, and $E_{\text{cell}} = 0$ (i.e., the system is at equilibrium).

In this lab you will construct a Daniell cell and a concentration cell and measure the cell potentials under non-standard states, and use these data to verify the Nernst equation.

Pre-Lab Questions

1. Consider the two half-reactions below:



- a) Find E° values for these half reactions from your textbook or other reference, and record them in the spaces provided above.
- b) Based on the E° values, provide the reactions below for a galvanic cell based on these half reactions.

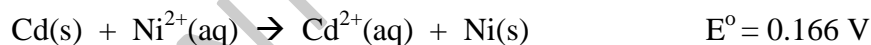
Anode half-reaction:

Cathode half-reaction:

Net cell reaction:

- c) Calculate the E°_{cell} for this galvanic cell.

2. Use the Nernst equation to calculate the cell potential, E_{cell} , for the following net cell reaction:



The cell conditions are $[\text{Ni}^{2+}] = 0.10 \text{ M}$ and $[\text{Cd}^{2+}] = 0.250 \text{ M}$ at 25°C . (All constants needed for this calculation can be found in the Introduction section. In order for units to cancel, it is useful to know that $1 \text{ Volt} = 1 \text{ Joule/coulomb}$.)

PROCEDURE

Part A. Evaluation of Nernst Equation

1. Label the two 50-mL beakers as “Zn” and “Cu.” Pour about 30 mL of 1.0 M $\text{Cu}(\text{NO}_3)_2$ solution into the 50-mL beaker labeled “Cu,” and about 30 mL of the $\text{Zn}(\text{NO}_3)_2$ solution into the “Zn” beaker.
2. Obtain a strip of filter paper. If the paper has not been pre-cut, cut a strip of filter paper about $\frac{1}{2}$ in. wide. Be sure the paper strip is long enough to reach between the two beakers with about $\frac{1}{2}$ in. of paper in the beaker solutions. **Do not allow the paper to come in contact with the solutions yet.**
3. Dip the strip of filter paper into the saturated KNO_3 solution. Remove the paper, and carefully wipe the excess solution from the paper. Place the wet filter paper between the two beakers, allowing about $\frac{1}{2}$ in. of paper to make contact with the solutions.
4. Obtain a piece of copper metal and a piece of zinc metal. Place the copper metal in the beaker containing the $\text{Cu}(\text{NO}_3)_2$ solution, and the zinc metal in the beaker containing the $\text{Zn}(\text{NO}_3)_2$ solution.
5. Connect the red lead (or positive) from the voltmeter to the copper electrode, and the black (negative) lead to the zinc electrode. At this point, your electrochemical cell should resemble the illustration in Figure 1.
6. Record the voltage reading from the voltmeter (in mV) on your Data Sheet. If the voltage reading is negative, reverse your leads to obtain a positive reading.
7. Disconnect the voltmeter leads from the electrodes and discard the filter paper.
8. Pipet 10-mL of the $\text{Cu}(\text{NO}_3)_2$ solution from the Cu beaker into the 50-mL volumetric flask. Fill the flask to the mark with deionized water, stopper the flask and mix well. At this point you may discard the copper solution remaining in the beaker, **but save the Zn (NO_3)₂ solution.** Clean and dry the Cu beaker.
9. Pour about 30 mL of the diluted $\text{Cu}(\text{NO}_3)_2$ solution into the Cu beaker.
10. Repeat Steps 2–7 using the diluted $\text{Cu}(\text{NO}_3)_2$ and the 1.0 M $\text{Zn}(\text{NO}_3)_2$ solutions, and record the cell potential on your Data Sheet.
11. Using the solution in the Cu beaker, perform a second dilution by repeating Step 8. Using this new solution, repeat Steps 2–7 and record the cell potential on the Data Sheet.
12. Perform two more dilutions by pipetting 10 ml of the solution in the Cu beaker into the 50 mL flask, repeating Steps 2–7 to obtain cell potentials for each dilution. Record all cell potentials on your Data Sheet.

Part B. Determining the Concentration of an Unknown Cu^{2+} Solution.

1. Clean and dry your Cu beaker. Obtain about 30 mL of the unknown copper solution and place it in the beaker.
2. Measure the cell potential of your electrochemical cell using this Cu solution, following the same procedure described in Part A. Record the voltmeter reading (in mV) on your Data Sheet.
3. Retain the beaker with your unknown Cu^{2+} solution for use in Part C. You may discard the $\text{Zn}(\text{NO}_3)_2$ solution in the Zn beaker. Clean and dry this beaker for use in Part C.

Part C. Potential of a Concentration Cell

1. Obtain about 30 mL of 1.0 M $\text{Cu}(\text{NO}_3)_2$ solution in your Zn beaker.
2. Following the same procedure described in Part A, construct a cell using these two copper solutions. **Be sure to use a copper electrode in both solutions!**
3. Be sure that the leads are connected to the electrodes to produce a positive voltage reading. Record the cell potential (in mV) on your Data Sheet.
4. Note which solution is in the anode half-cell (positive lead) and which solution is in the cathode half-cell (negative lead), and record this information on your Data Sheet.

Record the room temperature on your Data Sheet. If time permits, repeat Parts A–C.

CALCULATIONS

Part A.

1. Determine the concentration of Cu^{2+} in each of the copper solutions after dilution. The dilution equation is given below. The result of the first dilution is presented as an example.

$$M_1V_1 = M_2V_2$$

For the first dilution, you used 10.0 mL of a 1.0 M copper nitrate solution and diluted it to 50.0 mL. Therefore, $M_1 = 1.0 \text{ M}$, $V_1 = 10.0 \text{ mL}$, and $V_2 = 50.0 \text{ mL}$. Rearranging the dilution equation to solve for the new concentration is:

$$M_1V_1/M_2 = (1.0 \text{ M})(10.0 \text{ mL})/(50.0 \text{ mL}) = 0.20 \text{ M}$$

Calculate the concentration of the Cu solution after each dilution (M_2), using the concentration from the previous dilution as M_1 . Record these concentrations on your Data Sheet.

2. Using these $[\text{Cu}^{2+}]$ values, calculate $1/[\text{Cu}^{2+}]$ and $\ln(1/[\text{Cu}^{2+}])$ for each solution and record these results on your Data Sheet.
3. The appropriate form of the Nernst Equation for this cell is:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$$

Since the cell reaction always used a $[\text{Zn}^{2+}] = 1.0$, the above equation becomes:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \left(\frac{1}{[\text{Cu}^{2+}]} \right)$$

This equation takes the form of a straight line: $y = mx + b$. If we plot E_{cell} vs $\ln(1/[\text{Cu}^{2+}])$ we obtain a line with slope = $-(RT/nF)$ and an intercept = E_{cell}° .

4. Plot your E_{cell} data vs. $\ln(1/[\text{Cu}^{2+}])$.
5. From your plot, determine the slope and intercept of your line and record these values on your Data Sheet.
6. The theoretical intercept can be calculated as $E_{\text{Cu}}^{\circ} - E_{\text{Zn}}^{\circ}$, where the E° values are standard reduction potentials for the half reactions involving Cu and Zn. Using a table of standard reduction potentials, calculate the theoretical intercept and record this result on your Data Sheet.

7. The theoretical slope can be calculated by substituting in the appropriate values for R, T, and F; for this cell reaction, $n = 2$. Calculate the theoretical slope and record this value on your Data Sheet.

Part B.

1. Using your slope and intercept from Part A, calculate the value of $\ln(1/[\text{Cu}^{2+}])$ for your unknown solution. The equation is $y = mx + b$, where:

$$\begin{aligned} y &= \text{measured cell potential, } E_{\text{cell}} \\ b &= E^{\circ}_{\text{cell}}, \text{ from your plot in Part A} \\ m &= -(RT/nF) = \text{slope from your plot in Part A, and} \\ x &= \ln(1/[\text{Cu}^{2+}]) \end{aligned}$$

Once you have x, you can rearrange to find $[\text{Cu}^{2+}] = 1/e^x = e^{-x}$.

2. Record this value of x on your Data Sheet.

Part C.

1. For the concentration cell, the appropriate form of the Nernst equation is:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln \left(\frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}} \right)$$

Since the 1.0 M copper nitrate solution is placed in the cathodic cell, this reduces to:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln \left(\frac{[\text{Cu}^{2+}]_{\text{anode}}}{1} \right)$$

Furthermore, since we have the same half reaction in both the anodic and cathodic half cells, the value of $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0$. Now, the Nernst equation for the concentration cell reduces to:

$$E_{\text{cell}} = - \frac{RT}{nF} \ln [\text{Cu}^{2+}]_{\text{anode}}$$

Substituting values for $R = 8.314 \text{ J/mol}\cdot\text{K}$, $F=96486 \text{ coul/mol } e^{-}$, $n = 2$, and assuming $T = 298 \text{ K}$, we obtain a value for the pre-ln coefficient of 0.0128. Using the E_{cell} for your concentration cell (in Volts), you can calculate the value of $[\text{Cu}^{2+}]$ as:

$$[\text{Cu}^{2+}] = e^{-E_{\text{cell}}/0.0128}$$

Calculate the $[\text{Cu}^{2+}]$ for your unknown solution, and record this value on your Data Sheet.

Data Sheet

Part A.

Solution	[Cu ²⁺]	Voltage (mV)	1/[Cu ²⁺]	ln(1/[Cu ²⁺])
Trial 1:				
1	1.0 M			
2				
3				
4				
5				
Trial 2:				
1	1.0 M			
2				
3				
4				
5				

Attach your plots of E_{cell} vs $\ln(1/[\text{Cu}^{2+}])$ for trials 1 and 2.

	<i>Trial 1</i>	<i>Trial 2</i>	<i>Theoretical</i>
Slope =	_____	_____	_____
Intercept =	_____	_____	_____

Data Sheet

Part B.

	<i>Trial 1</i>	<i>Trial 2</i>
Cu ²⁺ Unknown ID:	_____	_____
E _{cell} (mV):	_____	_____
Unknown [Cu ²⁺]:	_____	_____

Part C.

	<i>Trial 1</i>	<i>Trial 2</i>
Cu ²⁺ Unknown ID:	_____	_____
E _{cell} (mV):	_____	_____
[Cu ²⁺] _{anode}	_____	_____
[Cu ²⁺] _{cathode}	_____	_____
Unknown [Cu ²⁺]:	_____	_____

Sample calculations:

Post-Lab Questions

1. Compare the results for your $[\text{Cu}^{2+}]$ unknown from the Daniell cell and the concentration cell:
 - a) What is the percent difference?
 - b) Which do you think is more accurate? Why?
2. If the temperature in the lab increased as you progressed through your dilutions for the Daniell cell investigation, how would this affect the slope and intercept of your E_{cell} vs. $\ln(1/[\text{Cu}^{2+}])$ plot?
3. Calculate the theoretical potential of a Daniell cell prepared with solutions of $[\text{Cu}^{2+}] = 0.50 \text{ M}$ and $[\text{Zn}^{2+}] = 0.05 \text{ M}$.
4. Instead of using Cu^{2+} and a Cu(s) electrode in the cathode half-cell, you use a solution of Sn^{2+} and a Sn(s) electrode. How would this affect the slope and intercept of your plot?