

Electrochemistry: Galvanic Cells And The Nernst Equation

The CCLI Initiative
Computers in Chemistry Laboratory Instruction

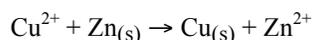
Learning Objectives

The objectives of this experiment are to

- construct galvanic cells and develop an electrochemical series based on potential differences between half-cells
- understand the Nernst Equation.

Background

Any chemical reaction involving the transfer of electrons from one substance to another is an oxidation-reduction (redox) reaction. The substance losing electrons is **oxidized** and the substance gaining electrons is **reduced**. Let us consider the following redox reaction:



This redox reaction can be divided into an oxidation and a reduction half-reaction:



A **galvanic cell** (Figure 1) is a device used to separate a redox reaction into its two component half-reactions in such a way that the electrons are transferred through an external circuit rather than by direct contact of the oxidizing agent

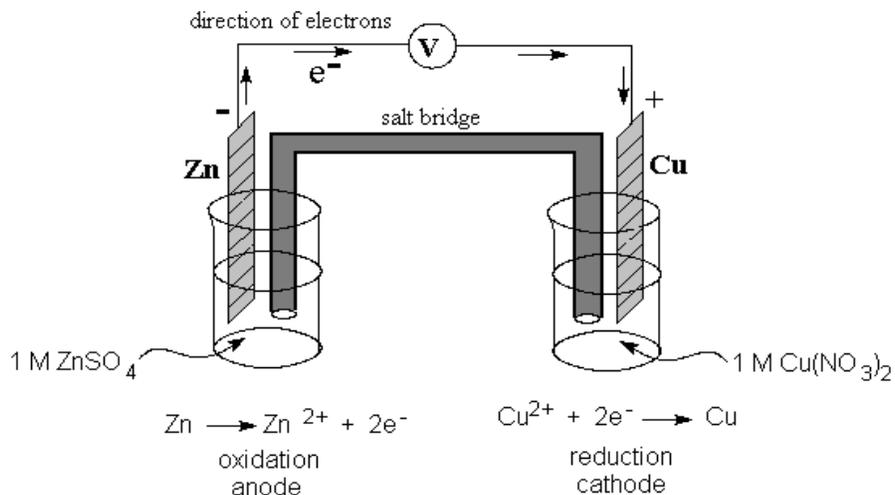


Figure 1. A Zinc/Cu Galvanic cell

and the reducing agent. This transfer of electrons through an external circuit is electricity.

Each side of the galvanic cell is known as a **half-cell**. For the redox reaction in Figure 1, each half-cell consists of an electrode (the metal of the half-reaction) and a solution containing the corresponding cation of the half-reaction. The electrodes of the half-cells are connected by a wire along which the electrons flow. In the cell, oxidation takes place at the zinc electrode, liberating electrons to the external circuit. Reduction takes place at the Cu electrode, consuming electrons coming from the external circuit.

- the electrode at which oxidation occurs is called anode.
- the electrode at which reduction occurs is called the cathode.

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Since oxidation releases electrons to the electrode, it is designated the negative electrode in the galvanic cell. Reduction removes the electrons from the cathode; it is the positive electrode. As zinc atoms are oxidized, the excess positive charge (Zn^{2+} ions) accumulates in solution around the zinc anode. Likewise, excess negative charge (NO_3^-) accumulates around the Cu cathode as Cu^{2+} ions are removed from the solution of $\text{Cu}(\text{NO}_3)_2$ by reduction to Cu metal. These excess charges create an electric field that causes the ions to migrate: positive ions (cations) migrate toward the cathode and negative ions (anions) migrate toward the anode. In order to make this flow of ions between the two half-cells possible, the cells are connected by a porous barrier (or salt bridge) through which the ions flow. The barrier prevents free mixing of the two solutions, but permits limited movement of ions so that the electrical neutrality is maintained in each half-cell.

Different metals, such as zinc and copper, have different tendencies to oxidize; similarly their ions have different tendencies to undergo reduction. The cell potential of a galvanic cell is due to the difference in tendencies of the two metals to oxidize (lose electrons) or their ions to reduce (gain electrons). Commonly, a reduction potential, a measure of electron affinity, is used to represent the relative tendency for a given metal ion to undergo reduction.

The voltage measured in the cell is the result of the two half-reactions. The magnitude of the potential depends on the concentrations of the ions, the temperature, and pressure of any gases. For instance, when all the concentrations in the Zn/Cu system are 1 molar and the temperature is 25°C , the cell voltage is +1.10 volts. It would be a monumental task to assemble a list of all possible cells and report their voltage. Instead we use the potential of the half-reactions. We cannot measure any half-cell potential directly, so we pick one half reaction, call it the standard, construct a cell, measure the cell voltage and report the potential relative to the standard. The standard that has been chosen by convention is:



Here the notation E° is called the standard electrode potential and is the assigned potential of the standard hydrogen electrode when the concentration of H^+ is 1 M and the pressure of the hydrogen gas is 1 atmosphere. The measured cell voltage using the standard hydrogen electrode is therefore the potential of the other half reaction.

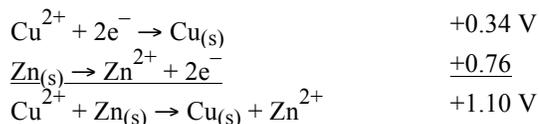
Tables of standard half-reaction potentials have been computed. The reactions by convention are written as reductions and hence the tables are called tables of standard reduction potentials. A brief example follows:

Some Standard Reduction Potentials at 25°C

Half-reaction	Potential (volts)
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.77
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}_{(\text{s})}$	+0.34
$2 \text{H}^+ + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})}$	0.00
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}_{(\text{s})}$	-0.13
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}_{(\text{s})}$	-0.14
$\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn}_{(\text{s})}$	-0.76
$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}_{(\text{s})}$	-2.37
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}_{(\text{s})}$	-3.05

The greater the tendency of the ion to gain electrons and undergo reduction, the less negative (or the more positive) the reduction potential. In the Cu/Zn cell, the Cu^{2+} has a greater tendency to undergo reduction than Zn^{2+} .

In the standard Cu/Zn cell the measured potential of 1.10 volts can be deduced from the sum of the potentials of the two half-reactions:



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Note: The sign of the standard reduction potential for the zinc half-reaction is reversed to give the potential of the oxidation half-reaction.

In Part I of this experiment, other metal/ion half-cell combinations will be tried. From the data, a table will be developed, listing 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 conditions (25°C, 1 M solution concentration, 1 atm gas pressure), these theoretically predicted voltages are known as **standard emfs (E° or E°_{cell})**.

In reality, standard 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 1800's while studying the thermodynamics of electrolyte solutions:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (2.303 RT/nF) \log(Q) \quad (11-1)$$

In equation (11-1), R is the gas constant (8.314 J mole⁻¹ K⁻¹), T is the temperature (Kelvin), 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]). If the reactions are carried out at room temperature (25°C), the Nernst equation becomes

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n) \log(Q) \quad (11-2)$$

Note in equations (1) and (2) that if the reaction quotient is equal to 1, then $E_{\text{cell}} = E^\circ_{\text{cell}}$.

In Part II of this experiment, voltages will be measured at various solution concentrations for the copper/zinc galvanic cell and compared with those calculated using the Nernst Equation.

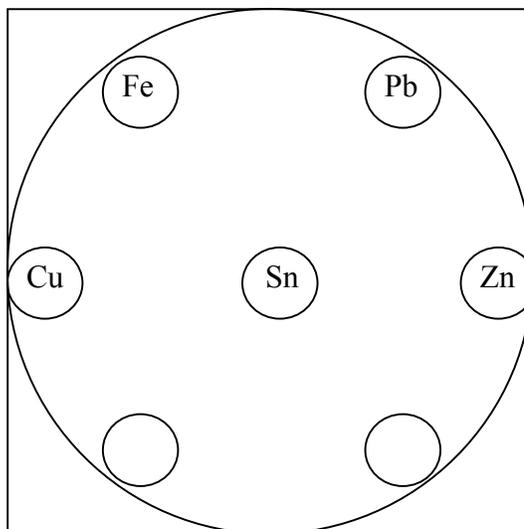
Safety Precautions

Safety goggles must be worn in the lab at all times. Any skin contacted by chemicals should be washed immediately.

Experimental Procedure

Part I: Galvanic Cells and the Electrochemical Series

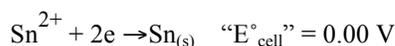
1. Turn on MicroLab and double click the MicroLab icon on the desktop. On the opening window for MicroLab select the Electrochemistry tab. From the experiment options highlight "hopechem". Read the text in the right hand window. Check that the CAT5 cable for voltage measurements is plugged in Input B (the cable has red and black alligator clips). Select OK to bring up the Experiment window.
2. Obtain an agar well plate, plastic cover and the container of metal electrodes. Identify the Cu, Pb, Sn, nichrome and Zn metal electrodes. The Sn will be more flexible than the Zn. Also, the Zn metal placed in a solution of Cu ions will quickly react and turn black. The Sn reacts only slowly.
3. The agar well plate and the plastic top should be labeled according to the diagram at the right, using pieces of tape on the plastic top and on the side of the agar well plate. Check the labels and alignment on both parts to see that they are consistent.
4. If necessary, clean one end of a metal electrode with sandpaper to remove any visible oxide layers, and rinse well with RO water (note that the nichrome wire is used for the Fe solution). Put a 90° bend in the electrode about 4 cm from the



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clean end. Place the electrode in the appropriate hole in the plastic top and wedge it in place with a #1 rubber stopper. The electrode should be placed such that when the top is placed on the well plate the clean end of the electrode will be in the middle of the respective well in the agar and about half-way down in the well.

- Repeat step 4 with each of the electrodes. When the set-up is complete, the top should be in place with each electrode held in place by a stopper while correctly positioned in the well. If necessary, make adjustments along the way. Have your instructor check the alignment when you have all five electrodes in place.
- Remove the plastic top and place it upside down on the lab bench so as not to change the position of the electrodes. Take the agar well plate to the side bench and use the dropping pipet found with each reagent bottle to add the appropriate 0.10 M metal ion solution to the wells. Note that the Fe solution is actually a mixture of Fe^{2+} and Fe^{3+} ions. The anion for all solutions is nitrate.
- The salt bridge needed to complete the circuit for each cell is "built into" the agar. The agar solution is 1% KNO_3 , such that the voltage can be measured between any two electrodes. Carefully place the plastic top on the well plate so all the electrodes are immersed in the correct solutions.
- The first set of voltage measurements will be made using the Sn as the reference electrode; this means that all cell voltages will be measured relative to the reduction of tin:



Connect the alligator clips to the Sn and Cu electrodes so that the observed voltage is positive (N.B. the interface display is in V). This is an arbitrary assignment, but it puts all the student data in a uniform format which makes reading the reports somewhat easier. Voltage meters are designed so that when the black lead (-) is connected to a "negative" electrode, or anode, and the red lead (+) connected to a positive electrode, or cathode, the displayed voltage will be positive. In this particular case, this means that the black lead should be connected to the Sn electrode. When recording measurements in your notebook indicate the observed voltage and which electrode was connected to the "black" lead and which electrode was connected to the "red" lead. Click **Start** to start the timer. To actually collect data, click Switch A. Only when Switch A is "on" will data be graphed or sent to the spreadsheet. Thus, only turn on Switch A after the leads have been connected to both electrodes. Collect data for about 30 – 40 seconds or until the signals seem to be quite stable (the voltage signal should not drift or change by more than about 2 mv (0.002 V) over this time interval). If the drift exceeds this, continue the measurement for another 30 - 40 seconds. When the signal is constant within 2 mv for the measured time interval, click Switch A "off" – no check mark – do not stop the experiment.

Connect the electrodes for the Sn/Pb combination (keep Sn black) and click Switch A on. Keep track of the time relative to the electrode combination so that you will know what voltages correspond to which electrode pairs. Collect data with the same criteria as above and click "off" Switch A when the signal appears stable (again do not select stop). Repeat the process for the Sn/Zn and Sn/Fe combinations – use switch A, not stop. Keep the same alligator clip on the Sn for all these measurements, since the Sn is the reference and the reference is a constant value. This set of data will be used to establish an Electrochemical Series which will be comparable to the Standard Reduction Potential Series. In your report this series will be used to predict voltages for other combinations of electrodes, whose actual voltages are measured in the following steps.

- Record the voltage for the Cu/Zn, Cu/Pb and Cu/Fe cells using the above procedure without selecting stop – use Switch A to control data collection. Keep the Cu electrode as the reference in each of these measurements. Indicate if the Cu reference is connected to the black (-) or red (+) terminal.
- Record the voltage for the Zn/Pb and Zn/Fe cells. Keep the Zn electrode as the reference in these measurements. Indicate if the Zn reference is connected to the black or red terminal.
- Record the voltage for the Pb/Fe cell. Indicate which electrodes are connected to the black and red terminals. After the measurements are completed, select Stop and "Save as" to store your data.
- Check with your instructor before you continue with this step. Connect the black and red alligator clips together. Pour the metal solutions from the wells directly from the agar well plate into the waste bucket. Fill a beaker with about 50 mL of RO water, gently pour this into the well plate to rinse the wells and pour the rinse

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into the waste bucket. Repeat this rinse twice more, but this rinse can go into the sink. Do not put the agar directly under running water, since it may break apart the gel. Disassemble the electrodes from the top plate and put the top plate on the agar well plate.

- For data analysis, left-click and drag to highlight a set of voltages (column B) in the spreadsheet. Right-click in the highlighted area to show a pop-up menu, select **Column Statistics** and record the average and standard deviation for the measured values. Record this voltage and standard deviation for each pair of electrodes.

Part II: The Nernst Equation

In this part of the experiment you will examine the effect of solution concentration on the cell voltage for the reaction



The Nernst equation allows calculation of the cell voltage E_{cell} as a function of the reactant and product concentrations. For the above reaction at 25°C, the Nernst equation is

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log\left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right) \quad (11.4)$$

Remember, solids and pure liquids are not included in the ratio of ([products]/[reactants]) given in the log term. Theoretically, E_{cell}° for the above reaction is 1.10 volts. Thus the value E_{cell} can be calculated knowing $[\text{Zn}^{2+}]$ and $[\text{Cu}^{2+}]$. In practice the value of E_{cell}° is treated as a constant k that is experimentally determined by measuring E_{cell} under conditions where the concentration of one ion is held constant and the concentration of the other ion is varied. Once the new constant k is known the measured voltage E_{cell} can be used to calculate an "unknown" concentration of the ion that had been varied. For this experiment the concentration of Zn^{2+} will be held constant and the Cu^{2+} will be varied, such that equation (10-4) will become

$$E_{\text{cell}} = k + \frac{0.0591}{2} \log([\text{Cu}^{2+}]) \quad (11-5)$$

The E_{cell}° and $[\text{Zn}^{2+}]$ do not appear in equation (11-5) because they are combined into the single constant term k . The sign of the log term is changed to + because the $[\text{Cu}^{2+}]$ in the log term is inverted in going from equation (11-4) to (11-5). Equation (11-5) has the form of a linear equation $y = mx + b$ where y is the experimentally measured E_{cell} and $\log [\text{Cu}^{2+}]$ is the x term. If the ideal Nernst behavior is observed the plot should have a slope of about 29.5 mv. The equation that is obtained using known $[\text{Cu}^{2+}]$ can then be used to measure an unknown $[\text{Cu}^{2+}]$ based on its observed E_{cell} .

There are 5 standard solutions of known Cu^{2+} concentration already prepared as indicated in the Table 1. In each case the indicated amount of the copper nitrate solution and potassium nitrate solution are added to the same 100 mL volumetric flask. While the variation in Cu^{2+} is the important aspect in this procedure, the addition of the potassium nitrate is needed to maintain the same total ionic charge in all solutions. This improves the quality of the measurements, but is not something you need to worry about in terms of any calculations. You need to calculate the last column of values in the table.

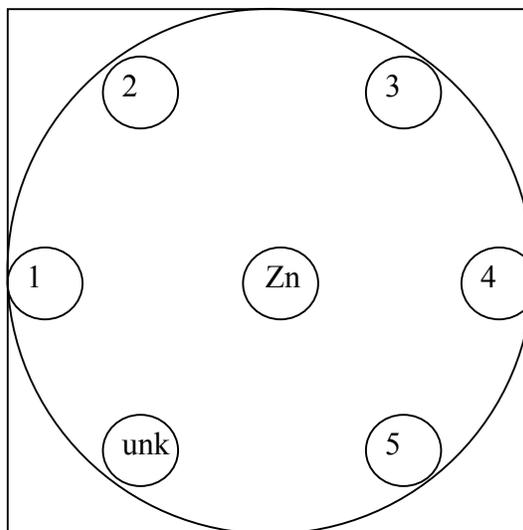
Solution #	mL $\text{Cu}(\text{NO}_3)_2$	mL 1 M KNO_3	Total mL	Final $[\text{Cu}^{2+}]$
#1	10 mL 1.00 M	0	100.0	
#2	3 mL 1.00 M	21.0	100.0	
#3	10 mL soln #1	27.0	100.0	
#4	10 mL soln #2	29.0	100.0	

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#5	10 mL soln #3	30.0	100.0	
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Table 1. Copper standards

1. Obtain an agar well plate, plastic cover, 6 copper electrodes and a Zn electrode.
2. The agar well plate and the plastic top should be labeled according to the diagram at the right, using pieces of tape on the plastic top and on the side of the agar well plate. Check the labels and alignment on both parts to see that they are consistent.
3. Take the Cu electrodes and a beaker of about 200 mL of RO water to the hood. In the hood you will find a 50 mL beaker with about 20 mL of con nitric acid. (CAUTION: con nitric acid is extremely corrosive). Place one end of the Cu wire in the HNO₃ and allow the wire to react for about 15 to 20 seconds. What do you observe? After you observe a reaction occurring at the wire remove it from the acid and drop it in the beaker of water. Clean all 6 Cu electrodes in this manner. Take the beaker containing the electrodes to the sink, pour off the RO water and add about 200 mL of fresh RO water. Do this rinse three times. The fourth time leave the electrodes in the beaker covered with about 100 mL RO water
4. If necessary, clean one end of the Zn electrode with sandpaper to remove any visible oxide layers, and rinse well with RO water. Put a 90° bend in an electrode about 4 cm from the clean end. Place the electrode in the appropriate hole in the plastic top and wedge it in place with a #1 rubber stopper (clean end in the well). The electrode should be placed such that when the top is place on the well plate the clean end of the electrode will be in the middle of the respective well in the agar and about half-way down in the well. Repeat this for all 6 copper and the one Zn electrode. Have your instructor check the alignment when all electrodes are in place.
5. Remove the plastic top and place it upside down on the lab bench so as not to change the position of the electrodes. Take the agar well plate to the side bench and use the dropping pipet found with each reagent bottle to add the appropriate zinc or standard copper ion solutions to the wells. The anion for all solutions is nitrate.
6. The salt bridge needed to complete the circuit for each cell is “built into” the agar. The agar solution is 1% KNO₃, such that the voltage can be measured between any two electrodes. Carefully place the plastic top on the well plate so all the electrodes are immersed in the correct solutions.
7. Connect the black lead from the interface to the Zn electrode and the red lead to the electrode in solution #1. Click **Start** to start the timer. To actually collect data, click Switch A. Only when Switch A is “on” will data be graphed or sent to the spreadsheet. Thus, only turn on Switch A after the leads have been connected to both electrodes. Collect data for about 30 – 40 seconds or until the signals seem to be quite stable (the voltage signal should not drift or change by more than about 2 mv (0.002 V) over this time interval). If the drift exceeds this, continue the measurement for another 30 - 40 seconds. When the signal is constant within 2 mv for the measured time interval, click Switch A “off” – no check mark – do not stop the experiment.
8. Switch the red lead to solution 2, click switch A “on” and collect data as indicated above. Set Switch A “off” – do not stop the program. Continue in this manner until all the voltages for all of the copper solutions have been measured. After the measurements are completed, select Stop and “Save as” to store your data.
9. Before you disassemble the electrode set-up, do a quick plot of voltage vs. log [Cu²⁺], which is equation 11-5. Check this with your instructor.
10. Once you get the OK for step 9, proceed as follows. Connect the black and red alligator clips together. Pour the metal solutions from the wells directly from the agar well plate into the waste bucket. Fill a beaker with



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about 50 mL of RO water, gently pour this into the well plate to rinse the wells and pour the rinse into the waste bucket. Repeat this rinse twice more, but this rinse can go into the sink. Do not put the agar directly under running water, since it may break apart the gel. Disassemble the electrodes from the top plate and put the top plate on the agar well plate.

11. For data analysis, left-click and drag to highlight a set of voltages (column B) in the spreadsheet. Right-click in the highlighted area to show a pop-up menu, select **Column Statistics** and record the average and standard deviation for the measured values. Record this voltage and standard deviation for each pair of electrodes.
12. Turn off the Microlab interface before leaving lab.

Lab Report Instructions:

This is the last of the quantitative laboratories for the year. You will need to hand in a report that includes a cover sheet, an experimental summary section (that includes both objectives of this lab), and a results and conclusions section. In the conclusion section, you should compare your experimental results to the results predicted from textbook values, and comment on any differences or similarities. As usual, comment on any possible sources of error in the measurements.

This word processed document should not exceed two pages in length. Attached to this document, you should have the spreadsheet and plot used to generate the Nernst equation plot (part II), and all the copies of lab notebook pages. The spreadsheet will also have the electrochemical series results (part I). In this table there must be a comparison to the expected values derived from the E° values listed in table 19-1 or Appendix F of your textbook. Be sure to answer all of the questions on page 11-9,10 and include this worksheet with your report.

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Experiment 11 Electrochemistry Worksheet

Part I.

1. Prepare a table that indicates the relative position of the half-reactions that you observed with respect to the Sn half-cell. Write each of the observed half-reactions as a reduction and place them in a table so that the reaction with *the most positive potential is at the top*. Include the Sn half-reaction and assign it a relative potential of zero (i.e., the potential of the Sn half-cell measured against itself). Include in the table the Standard Reduction Potential (SRP) for the half-reactions as found in Table 19.1 and Appendix F of your lecture textbook. Is your relative order for reduction potentials the same as that predicted by Standard Reduction Potentials? Comment in your narrative on any similarities or differences.

Reduction half-reaction	Potential in volts relative to Sn	*Potential in volts relative to hydrogen	SRP from text

*To calculate the voltages in this column, simply subtract 0.14V from the voltages in the column to the left (since the Sn electrode has a voltage of -0.137 V relative to the Standard Hydrogen Electrode).

2. Using data collected in items 7, 8, and 9 of Part I, complete the following table. Comment in your narrative report on any similarities or differences.

Cell	Measured Potential in volts	*Predicted Potential relative to Sn	**Predicted Potential based on SRP's
(a) Cu/Zn			
(b) Cu/Pb			
(c) Cu/Fe			
(d) Zn/Pb			
(e) Zn/Fe			
(f) Pb/Fe			

*To calculate the values in this column, use the voltages from the *second* column of the previous table.

**To calculate the values in this column, use the SRP's (the voltages from the *last* column of the previous table).

3. Write a balanced net ionic equation for the spontaneous overall reaction that occurred in each of the cells from the previous table in item 2:
 - a)
 - b)

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c)

d)

e)

f)

Part II.

1. Use the equation of the linear fit for the Nernst plot that you prepared in step 9 of Part II to report $[\text{Cu}^{2+}]$ in your unknown. Show your calculation.

2. What is the value of the slope from your plot? _____ What is the “ideal” slope from the Nernst Equation? _____ Comment on any differences or similarities.

3. Based on Eqns. 4 and 5, show how the intercept for the Nernst equation (k in the equation for item 1 above) can be used to obtain a value of E°_{cell} for the Cu/Zn system in this experiment. Recall that $[\text{Zn}^{2+}]$ was 0.1 M. Show your work. How does this calculated value of E°_{cell} compare with the three numerical values in Row 1 for Cu/Zn in the table in Part I, item 2 of this worksheet? Why does the measured value for the Cu/Zn potential represent E° for this cell? Comment on the comparisons.