# Experiment 9
# Electrochemistry I – Galvanic Cell

**Introduction:** Chemical reactions involving the transfer of electrons from one reactant to another are called *oxidation-reduction* reactions or *redox* reactions. In a redox reaction, two *half-reactions* occur; one reactant gives up electrons (undergoes oxidation) and another reactant gains electrons (undergoes reduction). A piece of zinc going into a solution as zinc ions, with each Zn atom giving up 2 electrons, is an example of an oxidation half-reaction.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \tag{1}$$

The oxidation number of Zn(*s*) is 0 and the oxidation number of the $Zn^{2+}$ is +2. Therefore, in this half-reaction, **the oxidation number increases**, which is another way of defining an oxidation. In contrast, the reverse reaction, in which $Zn^{2+}$ ions gain 2 electrons to become Zn atoms, is an example of reduction.

$$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s) \tag{2}$$

In a reduction there is a **decrease (or reduction) in oxidation number.** Chemical equation representing half-reactions must be both mass and charge balanced. In the half-reactions above, there is one zinc on both sides of the equation. The charge is balanced because the 2+ charge on the zinc ion is balanced by two electrons, $2e^{-}$, giving zero net charge on both sides.

Another example of reduction is the formation of solid copper from copper ions in solution.

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \tag{3}$$

In this half-reaction the oxidation number of the aqueous copper is +2, which decreases to 0 for the solid copper, and again charge and mass are balanced. However, no half-reaction can occur by itself. A redox reaction results when an oxidation and a reduction half-reaction are combined to complete a transfer of electrons as in the following example:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \tag{4}$$

The electrons are not shown because they are neither reactants nor products but have simply been transferred from one species to another (from Zn to $Cu^{2+}$ in this case). In this redox reaction, the Zn(*s*) is referred to as the *reducing agent* because it causes the $Cu^{2+}$ to be reduced to Cu. The $Cu^{2+}$ is called the *oxidizing agent* because it causes the Zn(*s*) to be oxidized to $Zn^{2+}$.

Any half-reaction can be expressed as a reduction as illustrated in the case where equation (1) can be reversed to equation (2). A measure of the tendency for a reduction to occur is its *reduction potential, E,* measured in units of **volts**. At standard conditions, 25 °C and concentrations of 1.0 *M* for the aqueous ions, the measured voltage of the reduction half-reaction is defined as the *standard reduction potential, E°.* Standard reduction potentials

have been measured for many half-reactions and they are listed in tables. A short list is also provided at the end of the In-Lab section. For the reduction half-reactions in equations (2) and (3), the standard reduction potentials are –0.76 V for zinc and +0.34 V for copper. The more positive (or less negative) the reduction potential, the greater is the tendency for the reduction to occur. So $Cu^{2+}$ has a greater tendency to be reduced than $Zn^{2+}$. Furthermore, Zn has a greater tendency to be oxidized than Cu. The values of $E°$ for the oxidation half-reactions are opposite in sign to the reduction potentials: +0.76 V for Zn and –0.34 V for Cu.

A *galvanic cell* or *voltaic cell* is a device in which a redox reaction, such as the one in equation (4), spontaneously occurs and produces an electric current. In order for the transfer of electrons in a redox reaction to produce an electric current and be useful, the electrons are made to pass through an external electrically conducting wire instead of being directly transferred between the oxidizing and reducing agents. The design of a galvanic cell (shown in Figure 1 for the equation (4) reaction) allows this to occur. In a galvanic cell, two solutions, one containing the ions of the oxidation half-reaction and the other containing the ions of the reduction half-reaction, are placed in separated compartments called *half-cells*. For each half-cell, the metal, which is called an *electrode*, is placed in the solution and connected to an external wire. The electrode at which oxidation occurs is called the *anode* [Zn in equation (4)] and the electrode at which reduction occurs is called the *cathode* [Cu in equation (4)]. The two half-cells are connected by a *salt-bridge* that allows a "current" of ions from one half-cell to the other to complete the circuit of electron current in the external wires. When the two electrodes are connected to an electric load (such as a light bulb or voltmeter) the circuit is completed, the oxidation-reduction reaction occurs, and electrons move from the anode (−) to the cathode (+), producing an electric current.
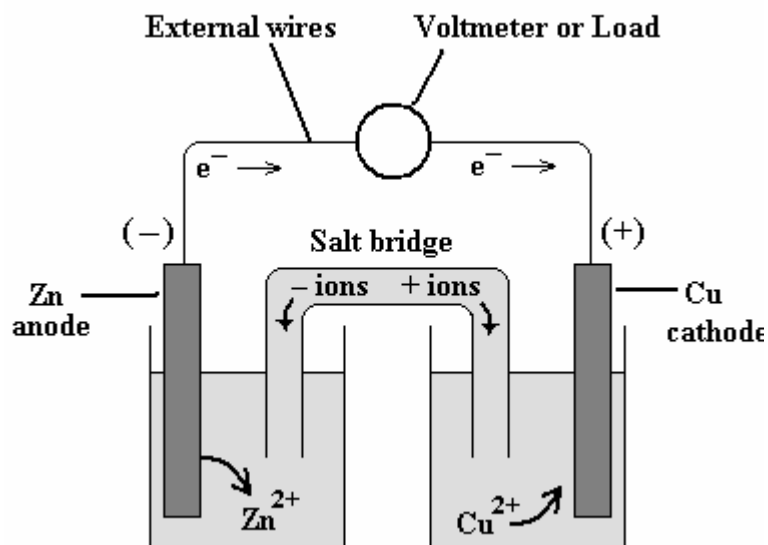


Figure 1. Galvanic cell (or battery) based on the redox reaction in equation (4).

The *cell potential*, $E_{cell}$, which is a measure of the voltage that the battery can provide, is calculated from the half-cell reduction potentials:

$$E_{cell} = E_{cathode} - E_{anode}$$

At standard conditions, indicated by the superscript º, the *standard cell potential*, $E°_{cell}$, is based upon the standard reduction potentials, as shown in equation (5).

$$E°_{cell} = E°_{cathode} − E°_{anode} \tag{5}$$

Based on the values for the standard reduction potentials for the two half-cells in equation (4) [–0.76 V for zinc anode and +0.34 V for copper cathode], the *standard cell potential*, $E°_{cell}$, for the galvanic cell in Figure 1 would be:

$$E°_{cell} = +0.34 \text{ V} − (−0.76 \text{ V}) = +1.10 \text{ V}$$

**The positive voltage for $E^0_{cell}$ indicates that at standard conditions the reaction is spontaneous.** Recall that $\Delta G° = − nFE°_{cell}$, so that a positive $E°_{cell}$ results in a negative $\Delta G°$. Thus the redox reaction in equation (4) would produce an electric current when set up as a galvanic cell.

When conditions are not standard, the *Nernst equation,* equation (6), is used to calculate the potential of a cell. In the Nernst equation, $R$ is the universal gas constant with a value of 8.314 J/(K·mol), $T$ is the temperature in K, and $n$ is the number of electrons transferred in the redox reaction, for example, 2 electrons in equation (4). $Q$ is the reaction quotient for the ion products/ion reactants of the cell. The solid electrodes have constant "concentrations" and so do not appear in $Q$. $F$ is the Faraday constant with a known value of 96,500 J/(V·mol).

$$E_{cell} = E^0_{cell} − \left(\frac{RT}{nF}\right)(\ln Q) \tag{6}$$

For our equation (4) example, $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, so $Q$ and $\ln Q$ are:

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad \text{and} \quad \ln Q = \ln [Zn^{2+}] − \ln [Cu^{2+}]$$

Since in equation (4), $n = 2$, the Nernst equation for this redox reaction becomes:

$$\boldsymbol{E_{cell}} = E^0_{cell} − \left(\frac{RT}{2F}\right)\ln[Zn^{2+}] + \left(\frac{RT}{2F}\right)\mathbf{ln[Cu^{2+}]} \tag{7}$$

In a series of galvanic cells, in which $[Zn^{2+}]$ is kept constant while $[Cu^{2+}]$ is varied, $\boldsymbol{E_{cell}}$ can be measured and it will be found to vary with $\mathbf{ln[Cu^{2+}]}$. A plot of the data obtained in which **y is $\boldsymbol{E_{cell}}$** and **x is $\mathbf{ln[Cu^{2+}]}$** will result in a straight line: y = mx + b. For equation (7), the terms $E°_{cell}$ and $−[RT/2F]\ln [Zn^{2+}]$ are constant and together they equal the intercept, b, of the line. $[RT/2F]$ will be the constant slope, m, provided the temperature is constant.

Thus a plot such as the one shown below can be generated by measuring the cell potential for different values of $[Cu^{2+}]$, while keeping $[Zn^{2+}]$ constant (at 1.0 $M$ in this plot). The equation of the line in this plot can then be used to determine ln $[Cu^{2+}]$ in a solution of unknown concentration from its measured $E_{cell}$, as long as $[Zn^{2+}]$ remains at 1.0 $M$ and the temperature at 25°C. This is the same principle used in a pH meter for the determination of $[H^+]$. Notice that as the concentration of $Cu^{2+}$ ion reactant increases (or $\ln[Cu^{2+}]$ becomes less negative), the potential of the cell increases.
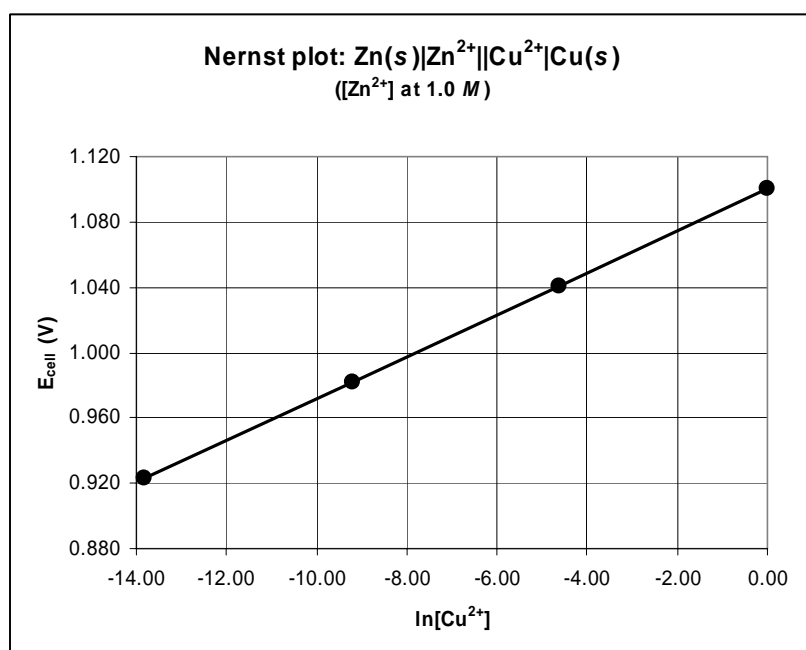


Figure 2. Nernst plot of $E_{cell}$ vs. ln $[Cu^{2+}]$ with $[Zn^{2+}]$ constant at 1.0 $M$. Note the standard cell notation in the graph title for the galvanic cell.

## Part A. Redox Reactions:

In this experiment you will observe several redox reactions in which metals are placed in solutions containing different metal ions. From your observations you will determine whether a redox reaction is occurring and write balanced redox equations for any that occur. For example, since as shown above, $Cu^{2+}$ has a greater tendency to be reduced than $Zn^{2+}$, you would expect that placing Zn metal into a solution of $Cu^{2+}$ ions would result in a direct redox reaction. $Cu^{2+}$ ions are reduced to Cu metal which is deposited on the Zn metal surface, while the Zn metal is oxidized to $Zn^{2+}$ ions which go into the solution. The redox equation for this reaction is therefore equation (4).

## Part B: Reduction Potentials:

You will then construct a series of three galvanic cells combining the zinc half-reaction with three different metal half-reactions (Cu, Fe and Pb). You will measure the cell potentials, $E°_{cell}$, using a Vernier voltage probe as shown in Figure 3. You will use 1.0 $M$ solutions for both half-cells, so Q = 1 and lnQ = 0 for the reaction. Thus the cell potential measured will be the same as $E°_{cell}$ as evident from the Nernst equation (6). You will then use your

measured $E°_{cell}$ values, the known zinc standard reduction potential, $E° = –0.76$ V, and equation (5) to calculate the $E°$ values for the three different half-reactions.

**Part C: Nernst Equation for varying Cu$^{2+}$ concentrations:**
Galvanic cells with different known Cu$^{2+}$ concentrations and a fixed Zn$^{2+}$ concentration will be prepared and their cell potentials measured. A plot of the Nernst equation, $E_{cell}$ vs. ln[Cu$^{2+}$], constructed from this data will then be used to find [Cu$^{2+}$] of an unknown solution.

**Part D: Determine the $E°$ for a voltaic cell using Cu and unknown metal:** Finally, you will measure the potential of a voltaic cell combining an unknown metal electrode with Cu ($E° = 0.34$ V). By measurement of the cell potential and use of equation (5), you will identify the unknown metal from its calculated value of $E°$. The unknown will have a more negative $E°$ than Cu, so the Cu will have a greater tendency to be reduced and thus will be the cathode when the $E°_{cell}$ is positive.

**Pre-Lab Notebook:** Provide a title, purpose, and a brief summary of the procedure in your lab notebook before coming to lab.

**Equipment:**

| | |
|---|---|
| 12-Well Microcell plate | Vernier LabPro |
| 24-Well Microcell plate | TI-84 Calculator |
| 1.00 mL Pipet | Vernier Voltage Probe |
| Pipet bulb | Steel Wool |
| 50 mL Beakers (5) | Filter paper strips |
| Forceps | 100.00 mL Volumetric flasks (3) |

**In Lab Procedure:**
Note: **Work in pairs**

**Part A. Redox Reactions:**
1.  Fill four cells in each of four columns of a 24-well microcell plate about three-fourths full with 1.0 *M* Cu(NO$_3$)$_2$, 1.0 *M* FeSO$_4$, 1.0 *M* Pb(NO$_3$)$_2$, and 1.0 *M* Zn(NO$_3$)$_2$ as shown in the diagram below.
2.  Polish small strips (4 each) of Cu, Fe, Pb and Zn with steel wool or sand paper and place them on a paper towel with written labels to insure that the metals are not mixed up with each other. Partially submerge the strips into the cell rows as shown below. Place only part of the metal into the solution so that any sign of a reaction (such as deposit of a metal on the submerged part of the strip) can be determined by comparison with the unsubmerged portion of the metal strip.

| | Cu(NO$_3$)$_2$ | FeSO$_4$ | Pb(NO$_3$)$_2$ | Zn(NO$_3$)$_2$ |
|---|---|---|---|---|
| Cu(*s*) | | | | |
| Fe(*s*) | | | | |
| Pb(*s*) | | | | |
| Zn(*s*) | | | | |

3. After 5 minutes examine each cell carefully to see if any **metal displacement redox reaction** has occurred. Record your observations in a table as shown above in your laboratory notebook. Then repolish and rinse the strips and return them to labeled paper towels located at the rear of the lab. If you are unsure about the identity of any strips, give them to your lab instructor.

**Part B: Reduction Potentials:**
1. Before constructing the galvanic cells, set up the Vernier system in DATAMATE with the voltage probe connected to channel 1 of the LabPro interface.
2. Hit CLEAR on the main screen of DATAMATE and the program will check for sensors. Once the voltage probe has been identified, and a reading near 0 volts is shown, you are ready to record data from the main screen. Obtain a 1.5 V battery from the instructor's desk and connect the red lead of the voltage probe to the (+) end of the battery (the cathode) and the black lead to the (−) end (the anode). If the voltage reading is not 1.5 V +/− 0.2 V, inform you instructor.
3. Wet a 2–3 inch long strip of filter paper with $KNO_3$ solution. Remove excess liquid gently (the paper easily rips when wet!) by blotting it on a paper towel and fold the paper into a U-shape; this will serve as your salt bridge. Place the salt bridge so that it will be immersed into each of two solutions in adjacent wells of a 12-well microcell plate (*see Figure 3 below*).
4. Construct a galvanic cell by adding solutions of 1.0 *M* $Cu(NO_3)_2$ as the aqueous $Cu^{2+}$ and 1.0 *M* $Zn(NO_3)_2$ as the aqueous $Zn^{2+}$ to the two adjacent wells. Do not immerse the copper and zinc at this time. Connect the leads from the voltage probe to the zinc and copper electrodes. **Recall that the red lead must be connected to the cathode and the black to the anode to obtain a positive cell voltage.**
5. Immerse the electrodes in the solutions and remove them in 5-10 seconds while avoiding contact with the salt bridge. If the voltage reading on the Vernier calculator is positive, the electrodes are connected correctly; if not, repolish and rinse the electrodes and reverse the connections.
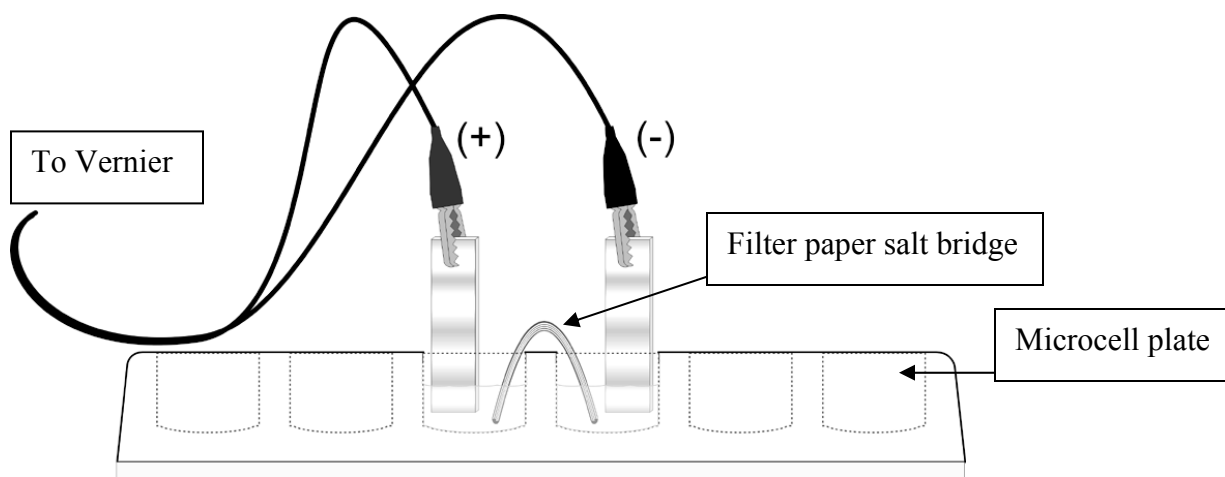


Figure 3. Galvanic cell apparatus for Part B.

6. Record the positive cell potential, in volts, in your laboratory notebook. *You will find that the voltage recorded is less than what you would expect based on standard reduction potentials. For example the Zn/Cu cell may be less than the 1.10 V calculated in the Introduction section. This is partly due to the presence of an oxide formed on one of the electrodes, a process which occurs very rapidly for easily oxidized metals and which changes the half-cell potential.*

7. Repeat steps 3-6 for galvanic cells of **Fe(in 1.0 *M* FeSO₄) - Zn** and **Pb(in 1.0 *M* Pb(NO₃)₂) - Zn.** Use a freshly prepared filter paper strip for the salt bridge of each cell.

**Part C: Nernst Equation for varying $Cu^{2+}$ concentrations:**
1. Prepare three dilute solutions of $CuSO_4$ by serial dilution from a 1.0 *M* $CuSO_4$ stock solution as follows: Transfer1.0 mL of 1.0 *M* $CuSO_4$ stock solution into a labeled (with tape) 100.00 mL volumetric flask and dilute to the mark with de-ionized water to form a 0.01 *M* solution. Rinse the pipet with a small volume of the solution to be transferred prior to use. Next take the 0.01 *M* solution just formed and transfer 1.0 mL of it into a labeled 100.00 mL volumetric flask. Dilute to the mark with de-ionized water to form the 0.0001 *M* solution. Repeat one more time so that you have the following set of solutions in labeled flasks:

   Solution A – 1 *M* $CuSO_4$ (stock solution)    Solution B – 0.01 *M* $CuSO_4$
   Solution C – 0.0001 *M* $CuSO_4$    Solution D – 0.000001 *M* $CuSO_4$
2. Prepare a half-cell of $Cu^{2+}$ by placing the copper solution D into a 12-microcell well.
3. Remove the copper and zinc electrodes from the half-cells used previously and clean and re-polish them.
4. Place 1.0 *M* $Zn(NO_3)_2$ in a cell next to the $Cu^{2+}$ half-cell. Connect the two half-cells with a freshly prepared salt bridge. Connect the copper and zinc electrodes to the correct voltage probe leads. Measure and record the cell potential in your laboratory notebook using the same technique (5-10 second immersion) with the voltage probe as in Part B.
5. Remove the $CuSO_4$ solution with a disposable pipet and repeat the measurement of $E_{cell}$ (steps 3-4) for the remaining three copper solutions in order of increasing concentration. Then, in the same way, measure the $E_{cell}$ for the unknown $Cu^{2+}$ solution. Record the measured values in a table as shown below in your notebook.

| Solution | D | C | B | A | Unknown |
|---|---|---|---|---|---|
| $[Cu^{2+}]$ | 0.000001 *M* | 0.0001 *M* | 0.01 *M* | 1.0 *M* | ? |
| Volts | | | | | |

**Part D: Determine the $E°$ for a voltaic cell using Cu and unknown metal:[1]**
1. Obtain a small amount of the unknown electrolyte solution labeled "1.0 *M* X ion" and the corresponding metal strip, "X". This metal is one of the metals in the table of Standard Reduction Potentials at the end of the In-Lab section.
2. Use a disposable pipet to transfer a small amount of 1.0 *M* X ion solution to a well adjacent to the 1.0 *M* $CuSO_4$ solution in a 12-microcell-test plate.
3. Make a new salt bridge by soaking a short length of filter paper in the $KNO_3$ solution.
4. Connect the X and Cu half-cells with the filter paper. Measure the positive potential of the X-Cu voltaic cell using the same technique as in Part B (**Red lead to the Cu**, which is the cathode).

5. After recording the potential once (5-10 seconds), remove both electrodes from the solutions and clean and polish each electrode. Set up the galvanic cell again. Connect the voltage probe as before.
6. Record the potential again. If the two measured potentials do not agree within .1 volts, test the galvanic cell a third time and record the potential immediately after making the connection with the voltage probe. Calculate the average of the measured potentials to use in the Post-Lab calculation.

Standard Reduction Potentials:

| Electrode | $E^o$ |
|---|---|
| $Ag^+ + e^- \rightarrow Ag$ | +0.80 V |
| $Cu^{2+} + 2e^- \rightarrow Cu$ | +0.34 V |
| $Pb^{2+} + 2e^- \rightarrow Pb$ | −0.13V |
| $Fe^{2+} + 2e^- \rightarrow Fe$ | −0.44 V |
| $Zn^{2+} + 2e^- \rightarrow Zn$ | −0.76 V |
| $Al^{3+} + 3e^- \rightarrow Al$ | −1.66 V |
| $Mg^{2+} + 2e^- \rightarrow Mg$ | −2.37 V |

**Literature Cited:**

1. *Advanced Chemistry with Vernier: Experiments for AP, IB, and College General Chemistry*, Jack Randall, Vernier Software and Technology, 2004, 20-1.

**Lab Report Outline for Electrochemistry I**

**Graded Sections of Report**                                                 **Percent of Grade**

Pre-Lab            10

In-Lab            10

Post-Lab

**Part A. Redox Reactions:**
For each of the metals, indicate the redox reactions you observed in a table as shown below. Write NR for (no reaction) where none was observed.     10

|  | $Cu(NO_3)_2$ | $FeSO_4$ | $Pb(NO_3)_2$ | $Zn(NO_3)_2$ |
|---|---|---|---|---|
| $Cu(s)$: |  |  |  |  |
| $Fe(s)$: |  |  |  |  |
| $Pb(s)$: |  |  |  |  |
| $Zn(s)$: | ** |  |  |  |

Explain your observations by calculating the $E^o$ for each reaction observed using equation (5) and values for the standard reduction potentials of the metals to determine why certain reactions are spontaneous (** *e.g.,* $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$, $E^0_{cell} = 1.10V$)     10

**Part B: Reduction Potentials:**
Report the cell potential for each galvanic cell and state which electrode corresponds to the cathode and which to the anode. Given $E^o = -0.76$ V for the $Zn^{2+}$ / Zn half-cell, and your measured $E^o_{cell}$, calculate the **reduction potential at the Cu, Fe, and Pb** cathodes     15

| Galvanic cell | $E_{cell}$, Volts | Cathode half-reaction | Anode half-reaction | Reduction Potential, volts |
|---|---|---|---|---|
| $Cu(s)$ - $Zn(s)$: |  |  |  |  |
| $Fe(s)$ - $Zn(s)$: |  |  |  |  |
| $Pb(s)$ - $Zn(s)$: |  |  |  |  |

1. Show a sample calculation for the case of the Fe(*s*) - Zn(*s*) cell.     5

**Part C: Nernst Equation:**
1. Construct and attach to your report a graph (similar to that shown in Figure 2) of the measured values of $E_{cell}$ versus $\ln[Cu^{2+}]$ from your data table.     5
2. Find the best fit line for the plot and state: "The equation of the line is _____".     5
3. From the equation for the line, determine $[Cu^{2+}]$ of the unknown solution. State: "The $[Cu^{2+}]$ of the unknown solution is _____."     10

**Part D: Determine the $E°$ for a voltaic cell using Cu and an unknown metal:[1]**
1.Use **equation (5)** to solve for $E°_{anode}$ of the unknown metal, keeping in mind that the Cu is the cathode for the cell when the $E°_{cell}$ is positive. Show the calculation of $E°_{anode}$. □     10
2. Compare the $E°_{anode}$ of the unknown to the values listed in the table given at the end of the In-Lab section and state: "The unknown metal is _____."     10