Matter and Motion Winter 2016
Lab 7: Electrochemistry of Galvanic Cells

Adapted from Mills, K.V., et al. Introducing Undergraduate Students to Electrochemistry: A Two-Week Discovery Chemistry Experiment. *J. Chem. Ed.* **2008**, *85*, 1116-1119

FORMAL LAB REPORT ***This is your POST-LAB assignment***

For the PRE-LAB, you should read the lab carefully and you may want to start writing/outlining your intro and your methods sections. All data and observations from lab will be initially recorded in your lab notebook as usual.

The lab write-up for this experiment is different from our previous assignments. The goal here is to work on the critical skill of communicating science through writing. The assignment for this lab is a formal, typed lab report that includes the following sections:

Introduction – The intro should contain all of the information needed for someone to understand your lab report. Consider your audience to be one of your peers who is “science-literate” but not familiar with electrochemistry (for example, yourself 1 week ago). In addition to clearly identifying what scientific questions you are attempting to answer with this experiment and why they may be of interest, the intro should be educational in that it provides concise yet thorough background information on the important concepts. Your background info should include, but not be limited to, redox reactions (how is electricity associated with these chemical reactions?), half-reactions, voltage (why do electrons go from one electrode to the other?), Galvanic cells (what are the necessary components? what determines the cell potential?), spontaneity, equilibrium, and reaction quotient in the context of galvanic cells, etc…

Methods – The methods section should be a detailed and very specific explanation of what you did and what you used to acquire your data. A person should be able to reproduce the experiment after reading your methods section. What chemicals did you use? What concentrations were your solutions? What instruments did you use? How many trials did you do and in what order? Etc…

Results and Discussion – The Results are your actual data; this includes figures of graphs, tables, or charts of your data and an explanation of what the data is. Each figure should be numbered and include a caption. Every figure must be referred to in the main body of the text. The Discussion is the analysis of your data and any associated calculations (what did you learn from the data, what does it mean, why is it important, etc…). Your Discussion should include possible answers to the scientific questions stated in the intro (there are three main questions to be answered here, see the Objectives). Be sure to include the reduction and oxidation half-reactions and the balanced overall reaction for the systems you investigated. What valuable information can you get from plotting E_{cell} vs ln(Q) for all of the class data? What does the slope tell you? What does the y-intercept tell you? Use this information to write a mathematical equation relating cell potentials and concentrations. How can you find determine the equilibrium concentrations and thus calculate the equilibrium constant? Did your prediction match your results for Part 2?

Conclusion - The conclusion should briefly summarize your results and highlight the main takeaway lessons from your analysis. The conclusion is also the place for proposing future work or additional scientific questions as related to the present experiment.

OTHER DETAILS: Please use a normal font style and size (11 or 12) and double space your report (this makes feedback much easier). Your lab report must include citations in ACS style. Here is one example style guide: http://library.williams.edu/citing/styles/acs.php. ***All writing must be in your own words and reflect your own learning. Please ask if you have any questions about citations and what constitutes plagiarism.

OBJECTIVES

1. To discover the relationship between the cell potential and the concentrations of reactants in an electrochemical cell.
2. To use this relationship to determine the equilibrium constant for the cell reaction.
3. To discover whether cell potentials are additive.

GENERAL BACKGROUND

In this experiment we focus again on the equilibrium process and measuring the equilibrium constant. In the Thermodynamics and Equilibrium Lab, we measured equilibrium constants by studying systems that are at equilibrium. In this experiment we will study systems that are not at equilibrium. We will measure the magnitude of the potential that is driving the system toward equilibrium. We will be able to calculate equilibrium constants that are very large or very small without actually measuring the extremely low concentrations of reactants or products that are associated with the equilibrium state of this type of system.

If a system is not in equilibrium there is a natural tendency for it to shift toward equilibrium. It is possible to obtain useful work from the system as it proceeds toward equilibrium. An electrochemical cell or battery is often used for this purpose. The manner in which an electrochemical cell can be used to derive useful work from a reaction proceeding to equilibrium is described in the following discussion of a simple battery.

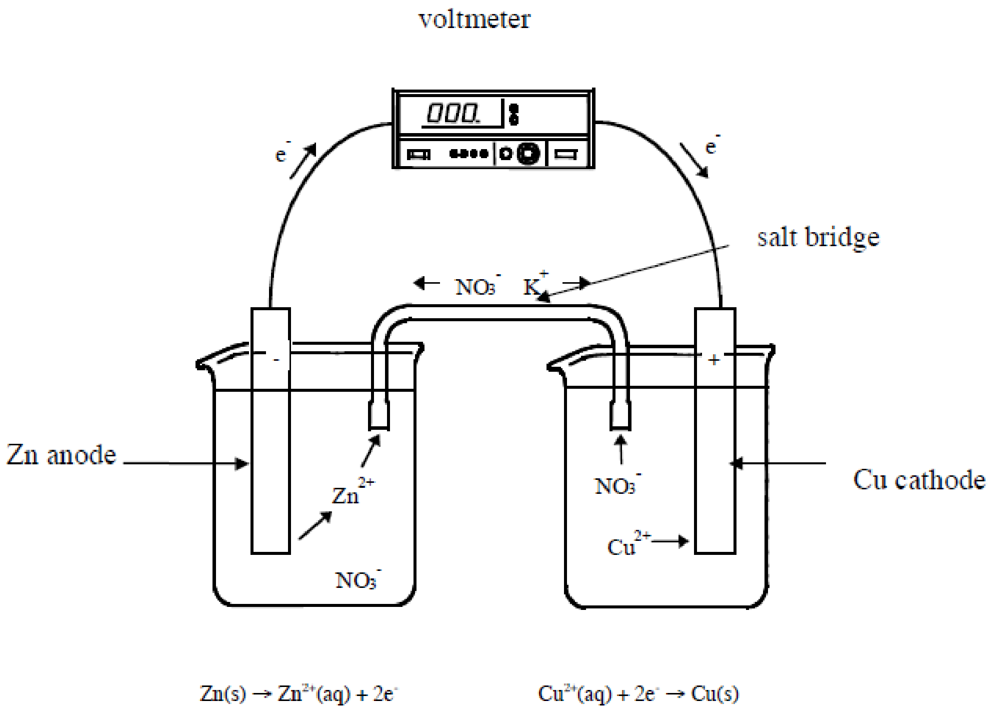
The reaction between solid Zn metal and ionic Cu^{2+} has a large equilibrium constant.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad K = 2 \times 10^{37}$$

It is reasonable to think of this oxidation/reduction reaction as being the combination of separate oxidation and reduction steps.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \text{ (oxidation)}$$
$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \text{ (reduction)}$$

Electrons are being removed from Zn and added to Cu^{2+}. Since electrons can be conducted through a wire it is possible to separate the sites of oxidation and reduction for this reaction and yet have the process occur. An appropriate design is shown below.



Both species involved in the oxidation process (Zn and Zn^{2+}) are present in one container (called the **oxidation half-cell**) while both species involved in the reduction process are present in the **reduction half-cell**. Electrons produced in the oxidation half-reaction are transported to the site of the reduction half-reaction via an electron conductor (a wire). A salt bridge of positive and negative ions also connects the half-cells to ensure that there is no build-up of charge in either cell. The tendency of the reaction to occur spontaneously produces what is called an **electric potential**. A voltmeter can measure the electric potential produced by the reaction. Electric potential (measured in voltage) is a measure of the maximum work that could be released per unit of charge passed through the cell. A volt is a joule (energy) per coulomb (charge). The voltage generated by a cell (often referred to as $\mathbf{E_{cell}}$) is related to how far the cell reaction is from equilibrium. One purpose of this experiment is to discover the relationship between the voltage of a cell and the position of the equilibrium for the reaction that produces the electromotive force (emf). This relationship can be derived from the expression that relates the cell voltage to the concentrations of the products and reactants of the cell reaction. It is this relationship that we will discover in our laboratory exercise.

It is reasonable there should be a dependence of cell voltage (or potential) on the concentration of reactants and products of the cell reaction. Increasing or decreasing the concentration of the reactants can control the direction of a chemical reaction. A non-spontaneous reaction can be made spontaneous by increasing the concentrations of reactants and decreasing the concentrations of products.

If we can determine the mathematical relationship between cell voltage (E_{cell}) and concentration of reactants and products we should be able to predict the concentrations that will give a cell voltage of zero. A cell voltage of zero suggests that there is no tendency for the cell reaction to go in either the forward or reverse direction. This suggests that the reaction has reached equilibrium.

BACKGROUND FOR PART 1

The goal of Part 1 is to discover the mathematical relationship between E_{cell} (cell voltage or emf) and the concentration of products and reactants in the cell reaction. This will then be used to derive an expression relating E_{cell} at standard states and the equilibrium constant K for the cell reaction.

You have been assigned a specific reaction to study. To simplify the experiment, we will work with an electrochemical cell in which the oxidation half-reaction is the same and only the reduction half of the reaction will be varied. The common oxidation half of the reaction will be the well-characterized and reproducible reaction shown below:

$$Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$$

The overall reaction that you will study will be the combination of this common half- reaction (we will call it our reference half-reaction) and the specific reduction system that you are assigned. Note that the reference oxidation reaction occurs within the electrode you will use. Specific procedures for each reduction system are found below. You will measure E_{cell} for a series of different concentrations of reactants and/or products. The manner in which you will construct your cell and prepare your solutions will be described in the pre-lab lecture. By appropriate graphical procedures you should be able to find the desired mathematical relationship for your system.

BACKGROUND FOR PART 2

In Part 1, we determined the values of E° (the intercept term in the Nernst equation) for a series of reactions carried out in an electrochemical cell. This gives us a relatively simple way to determine the equilibrium constant for any reaction for which we can design and construct an electrochemical cell. So, for example, when we put together a cell based on the half-reactions

$$Ag^+(aq) + e^- \rightarrow Ag(s) \quad \text{and} \quad Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$$

we can determine the K_{eq} for the reaction that is the sum of the two half-reactions, namely

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

An important point to recall is that the reaction is not actually allowed to go to completion in order to measure K_{eq}. E_{cell}, which is measured and used to determine $E°_{cell}$, is a measure of the tendency of the reaction to proceed toward equilibrium. By measuring $E°_{cell}$ we can calculate K_{eq} without the challenge of measuring the equilibrium concentrations of the reactants and products. These concentrations may be very small, which presents a severe experimental challenge.

Of course, our task still would be far from ideal if this were our only approach to determining equilibrium constants. It is not always easy to design a cell based on the reaction of interest. Further, the experimental procedure for accurately measuring $E°_{cell}$ is moderately time- consuming. In this part of the experiment we will use a limited number of experimentally measured $E°_{cell}$ values for reactions with a common oxidation half-reaction to predict the values of $E°_{cell}$ for a much larger set of reactions.

To consider how we might predict the value of $E°_{cell}$ for a reaction, refer to the five reactions studied in part 1. In each of the cells used there was a common half-cell. One of the half-cells was always based the oxidation of Ag in the presence of Cl^-:

$$Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$$

Because the reduction potentials for the five half-cells were determined relative to the same standard it might be possible to relate any of the five to each other. For example, from our work in part 1, we will determine that the reduction potential of a half-cell composed of 1.0 M Ag^+ and Ag wire relative to the reference is about 0.60 V while that of a corresponding $Cu^{2+}|Cu$ half-cell is about 0.10 V relative to the same reference. It is tempting to suggest that if the reduction potential of a $Ag^+|Ag$ half-cell were measured relative to a $Cu^{2+}|Cu$ half-cell (where the $Cu^{2+}|Cu$ half-cell now becomes the oxidation half-cell) we would obtain a value of 0.60 - 0.10 = 0.50 V. In other words, perhaps we can predict the values of E_{cell} or $E°_{cell}$ by evaluating the difference between the reduction potential of each of the half-reactions relative to a common reference.

An important implication is that we would be able to predict the potential of a cell that we did not construct. We would have the ability of calculating the equilibrium constant for additional reactions without performing additional experiments. In this case, we could calculate $E°_{cell}$ and equilibrium constant for the reaction

$$2\ Ag^+(aq) + Cu(s) \rightarrow 2\ Ag(s) + Cu^{2+}(aq).$$

Note that this reaction is the combination of the reduction half-reaction for Ag^+ and the oxidation half-reaction for Cu. This is consistent with our observation that the silver half-reaction had a greater reduction potential with respect to the reference electrode than did the copper half- reaction. To obtain the overall reaction in a balanced form we had to double the silver half- reaction and reverse the copper half-reaction. As shown below it is not necessary to double the reduction potential of the silver half-reaction despite the fact that the reaction is doubled since potential is an **intensive property** (voltage is joules per coulomb, and doubling the number of coulombs does change the joules per coulomb).

$$\begin{array}{ll} 2(Ag^+ + e^- \rightarrow Ag) & \mathbf{E}_{Ag^+/Ag} \\ \qquad Cu \rightarrow Cu^{2+} + 2\ e^- & -\mathbf{E}_{Cu^{2+}/Cu} \\ \hline 2\ Ag^+ + Cu \rightarrow 2\ Ag + Cu^{2+} & \mathbf{E}_{cell} = \mathbf{E}_{Ag^+/Ag} + (-\mathbf{E}_{Cu^{2+}/Cu}) \end{array}$$

PART 1 PROCEDURE

Note that you must test not only your assigned system in Part 1 but also perform all of Part 2, during which you work with another group to generate a new electrochemical cell.

Note: You are also asked to pre-calculate the first value for the reaction quotient, “Q,” for your assigned system. Clearly indicate this calculation in your notebook. Use the suggested headings in number 5 of each section below to help you track/organize the calculation. Note that $[Cl^-]$ is from the reference electrode; the molarity is 4.2M.

A. Ag^+/Ag System

1. Find the chemicals for this system.
2. Using a 100 mL volumetric flask, measure 100 mL of DI water and pour into a clean, dry 250 mL beaker. This will be your reaction beaker (or cathode).
3. Obtain approximately 50 mL of a 0.10 M stock $AgNO_3$ solution. Using the same 100 mL volumetric flask and the appropriate pipet, prepare a 1.0 x 10^{-3} M solution from this stock. Use DI water to dilute your stock solution to 100 mL. Mix well by inverting vigorously several times.
4. By pipet, measure 3 mL of the dilute solution from Step 3 and add to the reaction beaker in Step 2 and mix thoroughly. **Carefully** lower the reference electrode into the beaker until the tip is submerged. Attach a silver wire to the red alligator clip and place it in the reaction beaker. Turn the function knob on the meter to mV and take a reading. Continue adding with a pipet 3, 4, 5 and 5 mL of the dilute solution (mix thoroughly after addition) for a total volume of exactly 20 mL in 5 additions, taking mV readings after each addition. Then switch to the stock (0.1 M) solution, again adding 3, 3, 4, 5 and 5 mL up to a total stock volume of exactly 20 mL in 5 additions, taking mV readings after each addition. At the end, you should have a total of exactly 140 mL.
5. The following headings in your laboratory notebook will be helpful:
   mL of 1 x 10^{-3} M Ag^+ added , mL of 0.1 M Ag^+ added , Total Vol., Moles of Ag^+ added in this step, Total moles of Ag^+, Total $[Ag^+]$, $Q = 1/[Ag^+]\,[Cl^-]$, E_{cell} (V). Use this table to plot your data.

B. Cu^{2+}/Cu System

1. Find the chemicals for this system.
2. Add about 50 mL of DI water to the 100-mL volumetric flask. Measure 1 mL of 0.1 M nitric acid with a graduated cylinder and add to the volumetric. Make up to volume with DI water, shake well and pour into a clean, dry 250 mL beaker. This will be your reaction beaker (or cathode).
3. Obtain approximately 50 mL of a 1.0 M stock $Cu(NO_3)_2$ solution. Rinse the volumetric from step 2; using the appropriate pipet, prepare a 0.10 M solution from this stock. Use DI water to dilute your stock solution to 100 mL. Mix well by inverting vigorously several times.
4. By pipet, measure 3 mL of the dilute solution from Step 3 and add to the reaction beaker in Step 2 and mix thoroughly. **Carefully** lower the reference electrode into the beaker until the tip is submerged. Attach a copper wire to the red alligator clip and place it in the reaction beaker. Turn the function knob on the meter to mV and take a reading. Continue adding with a pipet 3, 4, 5 and 5 mL of the dilute solution (mix thoroughly after addition) for a total volume of exactly 20 mL in 5 additions, taking mV readings after each addition. Then switch to the stock (1.0 M) solution, again adding 3, 3, 4, 5 and 5 mL up to a total stock volume of exactly 20 mL in 5 additions, taking mV readings after each addition. At the end, you should have a total of exactly 140 mL.
5. The following headings in your laboratory notebook will be helpful:
   mL of 0.10 M Cu^{2+} added in this step, mL of 1.0 M Cu^{2+} added , Total Vol., Moles of Cu^{2+} added, Total moles of Cu^{2+} Total $[Cu^{2+}]$, $Q = 1/[Cu^{2+}][Cl^-]^2$, E_{cell} (V). Use this table to plot your data.

C. Fe^{2+}/Fe^{3+} System

1. Find the chemicals for this system.
2. Add about 50 mL of DI water to a 100-mL volumetric flask. Measure 1 mL of concentrated sulfuric acid with a graduated cylinder in the hood and add to the volumetric; also add by pipet 1 mL of 0.10 M $FeCl_3$ solution. Make up to volume with DI water, shake well and pour into a clean, dry 250 mL beaker. This will be your reaction beaker (or cathode).
3. Obtain approximately 50 mL of a 0.10 M stock iron (II) ammonium sulfate solution. Rinse the volumetric from step 2, and using the appropriate pipet, prepare a 1.0×10^{-3} M solution from this stock. Use DI water to dilute your stock solution to 100 mL. Mix well by inverting vigorously several times.
4. By pipet, measure 3 mL of the dilute solution from Step 3 and add to the reaction beaker in Step 2 and mix thoroughly. **Carefully** lower the reference electrode into the beaker until the tip is submerged. Attach a graphite rod to the end of the red alligator clip and place it in the reaction beaker. Turn the function knob on the meter to mV and take a reading. Continue adding with a pipet 3, 4, 5 and 5 mL of the dilute solution (mix thoroughly after addition) for a total volume of exactly 20 mL in 5 additions, taking mV readings after each addition. Then switch to the stock (0.1 M) solution, again adding 3, 3, 4, 5 and 5 mL up to a total stock volume of exactly 20 mL in 5 additions, taking mV readings after each addition. At the end, you should have a total of exactly 140 mL.
5. The following headings in your laboratory notebook will be helpful: mL of 1×10^{-3} M Fe^{2+} added , mL of 0.10 M Fe^{2+} added , Total Vol., Moles of Fe^{2+} added in this step, Total moles of Fe^{2+}, Total $[Fe^{2+}]$, Total $[Fe^{3+}]$, $Q = [Fe^{2+}]/[Fe^{3+}]\ [Cl^-]$, E_{cell} (V). Use this table to plot your data.

D. Quinhydrone System

1. Find the chemicals for this system.
2. Using a 100 mL volumetric flask, measure 100 mL of DI water and pour into a clean, dry 250 mL beaker. Using your spatula, add a small amount of solid quinhydrone (a 1:1 complex of quinine, Qu, and hydroquinone, H_2Qu) and stir constantly with a stirring rod until dissolved, and then add more until solid will not dissolve further, i.e., you have formed a saturated solution. This will be your reaction beaker (or cathode). Since quinhydrone is a 1:1 complex of Qu and H_2Qu, the saturated solution you are preparing has exactly the same molar amounts of Qu and H_2Qu, so the molar quantities can be cancelled from the reaction quotient equation, as indicated in #5 below.
3. Obtain approximately 50 mL of a 1.0 M stock HNO_3 solution. Using the same 100 mL volumetric flask and the appropriate pipet, prepare a 0.10 M solution from this stock. Use DI water to dilute your stock solution to 100 mL. Mix well by inverting vigorously several times.
4. By pipet, measure 3 mL of the dilute solution from Step 3 and add to the reaction beaker in Step 2 and mix thoroughly. **Carefully** lower the reference electrode into the beaker until the tip is submerged. Attach a graphite rod to the end of the red alligator clip and place it in the reaction beaker. Turn the function knob on the meter to mV and take a reading. Continue adding with a pipet 3, 4, 5 and 5 mL of the dilute solution (mix thoroughly after addition) for a total volume of exactly 20 mL in 5 additions, taking mV

readings after each addition. Then switch to the stock (1.0 M) solution, again adding 3, 3, 4, 5 and 5 mL up to a total stock volume of exactly 20 mL in 5 additions, taking mV readings after each addition. At the end, you should have a total of exactly 140 mL.

5. The following headings in your laboratory notebook will be helpful:
   mL of 0.10 M H^+ added , mL of 1.0 M H^+ added , Total Vol., Moles of H^+ added in this step, Total moles of H^+, Total $[H^+]$, $Q = [H_2Qu]/[Qu]\,[Cl^-]^2\,[H^+]^2$ (which reduces to $Q = 1/\,[Cl^-]^2\,[H^+]^2$), E_{cell} (V). Use this table to plot your data.

E. I_3^-/I^- System

1. Find the chemicals for this system.
2. Measure 1 mL of 0.010 M I_3^-/0.010 M I^- solution with a graduated cylinder and add to a 100 mL volumetric flask. Make up to volume with DI water, shake and pour into a clean, dry 250 mL beaker. This will be your reaction beaker (or cathode).
3. Obtain approximately 50 mL of a 1.0 M stock KI solution. Rinse the volumetric from step 2; using the appropriate pipet, prepare a 0.10 M solution from this stock. Use DI water to dilute your stock solution to 100 mL. Mix well by inverting vigorously several times.
4. By pipet, measure 3 mL of the dilute solution from Step 3 and add to the reaction beaker in Step 2 and mix thoroughly. **Carefully** lower the reference electrode into the beaker until the tip is submerged. Attach a graphite rod to the end of the red alligator clip and place it in the reaction beaker. Turn the function knob on the meter to mV and take a reading. Continue adding with a pipet 3, 4, 5 and 5 mL of the dilute solution (mix thoroughly after addition) for a total volume of exactly 20 mL in 5 additions, taking mV readings after each addition. Then switch to the stock (1.0 M) solution, again adding 3, 3, 4, 5 and 5 mL up to a total stock volume of exactly 20 mL in 5 additions, taking mV readings after each addition. At the end, you should have a total of exactly 140 mL.
5. The following headings in your laboratory notebook will be helpful:
   mL of 0.10 M I^- added , mL of 1.0 M I^- added , Total Vol., Moles of I^- added in this step, Total moles of I^-, Total $[I^-]$, Total $[I^-]^3$, Total $[I_3^-]$, $Q=[I^-]^3/\,[I_3^-]\,[Cl^-]^2$, E_{cell} (V) Use this table to plot your data.

STOP Come together as a class to share and graph your data when you finish Part 1.

PART 2 PROCEDURE

Are Cell Potentials Additive?

1. See the Half-Cell table below to prepare your assigned solution half-cell separately in a 100-mL volumetric, adding all extra solutions needed for your system. **(Note that dilution concentrations may be different from your Part 1 dilutions.)** Transfer this solution to a 250-mL beaker and get together with your partner group to measure your E_{cells} with the same meter and same reference electrode and then combine the two half-reactions.
2. Measure both of your half-cells with respect to the same reference electrode, using the proper sample electrode (silver wire, copper wire or graphite electrode) for each system. To measure the E_{cells} , place the cleaned reference electrode in each solution in turn and connect the red alligator clip to the sample electrode of each solution. Based on your measurements, determine which is the reduction half-cell (remember that you will subtract the E_{cell} of the oxidation half-cell from the E_{cell} of the reduction half-cell -both of which were measured with respect to the same reference).
3. Obtain a piece of string to be used as the salt bridge for the full cell you will construct together. First soak the string well in DI water, and then in about 20 mL of 1 M KNO_3 for several minutes.
4. Then connect the two cells, draping the soaked string into both beakers, making sure that one end of the string is well submerged in each beaker. ***(Do not allow the string to dry out while testing!)*** Check your prediction by measuring directly the E_{cell} of your full cell. To do this, detach the reference electrode from the black alligator clip, and then attach the black alligator clip to the sample electrode for the oxidation half- cell. Attach the sample electrode for the *red*uction half-cell to the *red* alligator clip (*red*uction=*red*). Turn the function knob to mV and record the reading.
5. What would happen if the red and black lead connections for this full cell were switched? Predict the potentials, and then test your theory. (When you are finished, remember to plug the reference electrode back in.)

PART 2

Prepare your diluted solution in a 100-mL volumetric, including any additional solutions.

$Ag^+ (aq) + e^- \rightarrow Ag(s)$
stock solution: 0.10 M $AgNO_3$
diluted/working solution: $[Ag^+] = 1 \times 10^{-2}$ M
sample electrode: Ag wire

$Cu^{2+} (aq) + 2 e^- \rightarrow Cu(s)$
stock solution: 1.0 M $Cu(NO_3)_2$
diluted/working solution*: $[Cu^{2+}] = 0.1$ M

*also include in volumetric 1 mL of 0.1 M HNO_3
sample electrode: Cu wire

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
stock solution: 0.10 M $(NH_4)_2Fe(SO_4)_2$
diluted/working solution*: $[Fe^{2+}] = 1 \times 10^{-2}$ M

*also include in volumetric 1 mL of conc. sulfuric acid and 1 mL of 0.10 M $FeCl_3$
sample electrode: graphite rod

$Qu(aq) + 2 H^+ (aq) + 2 e^- \rightarrow H_2Q (aq)$
stock solution: 1.0 M HNO_3
diluted/working solution: $[H^+] = 0.1$ M after prep., add solid quinhydrone to saturate

sample electrode: graphite rod

$I_3^-(aq) + 2 e^- \rightarrow 3 I^-(aq)$
stock solution: 1.0 M KI
diluted/working solution*: $[I^-] = 0.1$ M

*also include in volumetric 1 ml of 0.01 M I_3^-/0.01 M I^- (Be sure to include in your calculations of “Q”)
sample electrode: graphite rod