Investigation 3: Electrochemistry; Spontaneous Reactions and Equilibrium Constants

Focus Questions: *What is the relationship between cell potential and concentrations of reactants in an electrochemical cell? Are cell potentials additive? How are equilibrium constants related to cell potential?*

Pre-lab required reading

Chemistry; an Atom-Focused Approach: Sections 17.2 – 17.6

Primers:
          Electrochemistry primer
          Volumetric glassware use – General
          Volumetric glassware use – volumetric flask
          Volumetric glassware use – volumetric pipet
          Volumetric glassware use – micropipette

Safety and Waste Disposal

- Solutions of quinone, hydroquinone, iron(II) ammonium sulfate, potassium iodide, and potassium nitrate are irritants.
- Solutions of copper(II) nitrate, iodine, iron(III) chloride, silver nitrate and sulfuric acid are corrosive.
- Solutions of iodine, sulfuric acid and nitric acid are toxic.
- Solutions of iodine are lachrymators.
- Solutions of copper (II) nitrate, nitric acid, potassium nitrate, silver nitrate and sulfuric acid are oxidizers.
- Googles, gloves and appropriate lab attire should be worn at all times
- All solutions used in this lab should be disposed of as hazardous waste in the appropriate container.

Background

In this experiment we will study systems that are not at equilibrium with the goal of determining what conditions are required for them to be at equilibrium. We will measure the magnitude of the potential (ΔG) that is driving the system toward equilibrium by measuring a voltage and relating that to the difference in Gibb's free energy. This strategy allows us to measure the equilibrium conditions for reactions that are mostly products or mostly reactants at equilibrium.

If a system is not at 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 and the work that is done is electrical work. The manner in which an electrochemical cell can be used to derive electrical work from a reaction proceeding to equilibrium is described in detail in the electrochemistry primer.

Part I: The relationship between E_{cell} and concentrations of reactants and products

The goal of Part I is to discover (or confirm) 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:

        $Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$
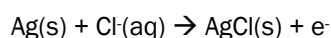
The overall reaction that you will study will be the combination of this common half-reaction (we will call it our reference half-reaction) and the specific reduction system that you are assigned. Note that the reference oxidation reaction occurs within the pH electrode you will use as a reference electrode. 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 by your instructor. By appropriate graphical procedures you should be able to find the desired mathematical relationship for your system.

Part I: 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. **Important: You must pre-calculate all values for the reaction quotient, "Q", and include these values for your assigned system in your notebook. This is most easily done using a spreadsheet with columns that contain the information in the suggested headings in number 4 of each section below to help you track/organize the calculation. Note that the [Cl⁻] is from the reference electrode; the molarity is 4.2 *M*.** The supplies and stock solution needed for your assigned system will be at the station where your group normally works.

A. Ag⁺/Ag system
   1. Using a 100 mL graduated cylinder, measure 100 mL of E-pure water and pour into a clean, dry 250 mL beaker. This will be your reaction beaker (or cathode). Place this beaker on the stir station and use the magnetic stir bar to stir the "solution". Make sure the lead with both a black and a red alligator clip is plugged into the Vernier LabQuest on channel 2. The pH electrode should be plugged into the Vernier LabQuest on channel1 and clamped to the ring stand on the stir station. Attach the red lead to the sliver wire provided (The black lead can be left disconnected). Open the LabQuest software and set up an experiment for single events with entry. Label the entry column "Q".
   2. Use a 100 mL volumetric flask and the appropriate glass pipet to prepare a 0.01 M solution from the 0.1 M stock AgNO₃(aq) solution provided. Use E-pure water to prepare your solution.
   3. By glass pipet, measure 3 mL of the dilute solution (0.01 M) from step 2 and add to the reaction beaker in step 1 while the solution is stirring. Turn off the stir bar magnet and wait until the stir bar stops spinning. **Carefully** lower the silver wire and the reference pH electrode into the beaker until the tip is submerged. Once the voltage reading has stabilized, click the button in the software to "keep" that point. You will be prompted to enter your previously calculated value of Q for this first addition. Continue adding with the appropriate glass pipet 3, 4, 5 and 5 mL of the dilute (0.01 M) solution (mix thoroughly after each addition being careful not to hit the reference pH electrode with the stir bar). Record the voltage and enter the value of Q for 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 would have a total of exactly 140 mL in your reaction beaker. **DO NOT DISCARD YOUR HALF CELL AS YOU WILL NEED IT FOR PART II.**
   4. The following headings in your laboratory notebook (and spreadsheet calculation of Q) will be helpful:
   mL of 0.01 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). If the plot that is generated by LabQuest is not linear, transform the data to obtain a linear plot. Find the equation of best fit for your linear plot.

B. Cu⁺²/Cu system
   1. Add about 50 mL of E-pure water to the 100-mL volumetric flask. Measure 1mL of 0.1 M nitric acid with a graduated cylinder and add to the 100-mL volumetric flask.   Dilute to the mark with E-pure water, mix well and pour into a clean, dry 250 mL beaker. This will be your reaction beaker (or cathode). Place this beaker on the stir station and use the magnetic stir bar to stir the "solution". Make sure the lead with both a black and a red alligator clip is plugged into the Vernier LabQuest on channel 2. The pH electrode should be plugged into the Vernier LabQuest on channel1 and clamped to the ring stand on the stir station. Attach the red lead to the copper wire provided (The black lead can be left disconnected). Open the LabQuest software and set up an experiment for single events with entry. Label the entry column "Q".
   2. Use a 100 mL volumetric flask and the appropriate glass pipet to prepare a 0.10 M solution of Cu(NO₃)₂(aq) from the 1.0 M stock. Use E-pure water to prepare your solution.
   3. By glass pipet, measure 3 mL of the dilute solution (0.1 M) from step 2 and add to the reaction beaker in step 1 while the solution is stirring. Turn off the stir station and wait until the stir bar has stopped spinning. **Carefully** lower the Cu electrode and the reference electrode into the beaker until the tip is submerged.

Once the voltage reading has stabilized, click the button in the software to "keep" that point. You will be prompted to enter your previously calculated value of Q for this first addition. Continue adding with a glass pipet 3, 4, 5 and 5 mL of the dilute (0.1 M) solution (mix thoroughly after each addition being careful not to hit the reference pH electrode with the stir bar). Record the voltage and enter the value of Q for 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 would have a total of exactly 140 mL in your reaction beaker. **DO NOT DISCARD YOUR HALF CELL AS YOU WILL NEED IT FOR PART II.**

4. The following headings in your laboratory notebook (and spreadsheet calculation of Q) will be helpful: mL of 0.1 M Cu^{+2} added, mL of 1.0 M Cu^{+2} added, Total Vol., Moles of Cu^{+2} added in this step, Total moles of Cu^{+2}, Total $[Cu^{+2}]$. $Q = 1/[Cu^{+2}][Cl^-]^2$, E_{cell} (V). If the plot you obtain in LabQuest is not linear, transform the data to give a linear plot. Find the equation of best fit for your linear plot.

C. Quinhydrone system
1. Using a 100 mL graduated cylinder, measure 100 mL of E-pure water and pour into a clean, dry 250 mL beaker. Place the beaker on the stir station. Using your spatula, add a small amount of solid quinhydrone (a 1:1 complex of quinone (Qu) and hydroquinone (H_2Qu)) and stir constantly to dissolve, 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). Make sure the lead with both a black and a red alligator clip is plugged into the Vernier LabQuest on channel 2. The pH electrode should be plugged into the Vernier LabQuest on channel1 and clamped to the ring stand on the stir station. Attach the red lead to the graphite rod provided (The black lead can be left disconnected). Open the LabQuest software and set up an experiment for single events with entry. Label the entry column "Q". 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 # 4 below.
2. Using a 100 mL volumetric flask and the appropriate glass pipet, prepare a 0.10 M solution of HNO_3 from the 1.0 M stock. Use E-pure water to prepare your solution.
3. By glass pipet, measure 3 mL of the dilute solution from step 2 and add to the reaction beaker in step 1 while the solution is stirring. Turn off the stir station and wait until the stir bar has stopped spinning. **Carefully** lower the graphite and the reference electrode into the beaker until the tip is submerged. Once the voltage reading has stabilized, click the button in the software to "keep" that point. You will be prompted to enter your previously calculated value of Q for this first addition. Continue adding with a glass pipet 3, 4, 5 and 5 mL of the dilute (0.1 M) solution (mix thoroughly after each addition being careful not to hit the reference pH electrode with the stir bar). Record the voltage and enter the value of Q for 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 would have a total of exactly 140 mL in your reaction beaker. **DO NOT DISCARD YOUR HALF CELL AS YOU WILL NEED IT FOR PART II.**
4. The following headings in your laboratory notebook (and spreadsheet to calculate Q) 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 $[H^+]$. $Q = [H_2Qu]/[Qu][H^+]^2[Cl^-]^2 = 1/[H^+]^2[Cl^-]^2$, E_{cell} (V). If the plot you obtain in LabQuest is not linear, transform the data to give a linear plot. Find the equation of best fit for your linear plot.

D. I_3^-/I^- system
1. Using a graduated cylinder, measure 1 mL of 0.010M I_3^-/0.010 M I^- solution into a 100-mL volumetric flask. Use E-pure water to dilute to the mark, mix well and pour into a clean, dry 250 mL beaker. This will be your reaction beaker (or cathode). Make sure the lead with both a black and a red alligator clip is plugged into the Vernier LabQuest on channel 2. The pH electrode should be plugged into the Vernier LabQuest on channel1 and clamped to the ring stand on the stir station. Attach the red lead to the graphite rod provided (The black lead can be left disconnected). Open the LabQuest software and set up an experiment for single events with entry. Label the entry column "Q".
2. Use a 100 mL volumetric flask and use the appropriate glass pipet to prepare a 0.10 M solution of KI(aq) from the 1.0 M stock. Use E-pure water to prepare your solution.
3. By glass pipet, measure 3 mL of the dilute (0.10 M) solution from step 2 and add to the reaction beaker in step 1 while stirring. Turn off the stir station and wait until the stir bar has stopped spinning. **Carefully** lower the graphite and the reference electrode into the beaker until the tip is submerged. Once the voltage reading has stabilized, click the button in the software to "keep" that point. You will be prompted to enter your previously calculated value of Q for this first addition. Continue adding with a glass pipet 3, 4, 5 and 5 mL of the dilute (0.1 M) solution (mix thoroughly after each addition being careful not to hit the reference

pH electrode with the stir bar). Record the voltage and enter the value of Q for 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 would have a total of exactly 140 mL in your reaction beaker. **DO NOT DISCARD YOUR HALF CELL AS YOU WILL NEED IT FOR PART II.**

4. The following headings in your laboratory notebook (and spreadsheet for calculating Q) 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 $[I_3^-]$. $Q = [I^-]^3/[I_3^-][Cl^-]^2$, E_{cell} (V). If the plot you obtain in LabQuest is not linear, transform the data to give a linear plot. Find the equation of best fit for your linear plot.

Part II: Are cell potentials additive?

In Part 1, we determined the values of E^o (the intercept 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 (see electrochemistry primer for details). So, for example, when we put together a cell based on the half-reactions

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

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

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
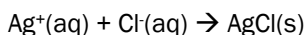
An important point to recall is that the reaction is not actually allowed to go to completion in order to measure K_{eq}. E_{cell}, which is measured and used to determine E^o_{call}, is a measure of the tendency of the reaction to proceed toward equilibrium. By measuring E^o_{cell} we can calculate 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^o_{cell} is moderately time-consuming. In this part of the experiment we will use a limited number of experimentally measured E^o_{cell} values for reactions with a common oxidation half-reaction to predict the values of E^o_{cell} for a much larger set of reactions.

To consider how we might predict the value of E^o_{cell} for a reaction, refer to the four 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 on the oxidation of Ag in the

$Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$
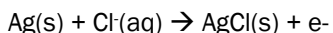
Because the reduction potentials for the four half-cells were determined relative to the same standard it might be possible to relate any of the four to each other. For example, from our work in part 1, we will determine that the reduction potential of a half-cell composed of 1.0 M Ag^+ and Ag wire relative 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 the $Ag^+|Ag$ half-cell were measured relative to the $Cu^{2+}|Cu$ half-cell (where $Cu^{2+}|Cu$ 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^o_{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^o_{cell} and equilibrium constant for the reaction

$2 Ag^+(aq) + Cu(s) \rightarrow 2 Ag(s) + Cu^{2+} (aq)$.
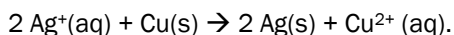
Note that this reaction is the combination of the reduction half-reaction for Ag^+ and the oxidation half-reaction for Cu(s). This is consistent with our observation that the silver half-reaction had a greater reduction potential with respect to the reference electrode than did the copper half-reaction. 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**.

Part II Procedure: Are cell potentials additive?
Find two other groups that studied a different system than your group. Using the final solution from Part I, complete the following for each combination of cells
1. 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_{cell}, 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).
2. Obtain a piece of string that has been soaking in a solution of 1 M KNO_3(aq).
3. 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 predictions 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 reduction half-cell to the red alligator clip (reduction = red).
4. What would happen if the red and black lead connections for this full cell were switched? Predict the potentials, and then test your theory.

References
Atkins, P.; Jones, L. "Chemical Principles: The Quest for Insight", 5th ed.; Freeman: New York. **2010**.

Mills, Kenneth V., Herrick Richard, S. Guilmette, Louise W., Nestor, Lisa P., Shafer, Heather, and Ditzler, Mauri A., *Introducing Undergraduate Students to Electrochemistry: A Two-Week Discovery Chemistry Experiment.* J. Chem. Ed. **85** (2008) 1116-1119.