Experiment 5
Electrochemistry[1]

Due to impending cutbacks at CSI you are searching for a new position. You are delighted to hear of the proposed production of an exciting new television series entitled *Survival Island*, a cross between the current hit *Survivor* and the classic favorite *Gilligan's Island*. You are even more delighted to hear of try-outs for a "Professor" character. Considering your outstanding qualifications as a chemistry consultant at CSI and your winning personality, this may be the ideal job for you. The producers are looking for a "Professor" who will be able to work such miracles as producing a coconut-cream pie without any sources of dairy products or electricity for an oven. In order to find the best Professor, the producers and their scientific consultants have created the following test of chemical credentials. Because not all candidates have the exemplary educational qualifications that you have, the producers are supplying everyone with the same background material from which to work. The interview will consist of pre-interview tasks, experimental lab work, and a written report summarizing that lab work.

Electrochemical Theory needed for Professor Interview

An electrochemical (or *galvanic*) cell, also known as a battery, is a device that produces an electric current as the result of an electron transfer reaction. Such electron transfer reactions are also known as oxidation-reduction, or redox, reactions. Electron transfer occurs as one substance is oxidized, or loses electrons, while another substance is reduced, or gains electrons. For example, if a piece of zinc metal were immersed in a solution containing copper(II) ions, the zinc would spontaneously lose electrons while the Cu(II) would spontaneously gain electrons. This process can be expressed as two half-reactions that sum to yield the overall reaction:

1st half rxn. $Zn\ (s) \rightarrow Zn^{+2}\ (aq) + 2\ e^-$

2nd half rxn. $Cu^{+2}\ (aq) + 2\ e^- \rightarrow Cu\ (s)$

overall net rxn. $Zn\ (s) + Cu^{+2}\ (aq) \rightarrow Cu\ (s) + Zn^{+2}\ (aq)$

Any spontaneous redox reaction can be harnessed to produce electrical energy under the right conditions. The problem with simply dropping a piece of zinc metal into a solution of Cu(II) is that the electrons provided by the zinc move directly to the aqueous Cu(II) ions without doing any work. In order to create a useful battery, the two half reactions must be physically separated so that the electrons will flow through an external circuit as shown in Figure 1. A salt bridge is necessary for charge balance: in this case sulfate ions flow from the copper to the zinc compartment.

The electrochemical cell shown in Figure 1 can be represented by the following shorthand:

$$Zn\ (s)\ |\ Zn^{+2}\ (aq)\ ||\ Cu^{+2}\ (aq)\ |\ Cu\ (s)$$

[1] Adapted from Chemistry The Central Science, Laboratory Experiments, 6th Edition, by J.H. Nelson and K.C. Kemp and Laboratory Inquiry in Chemistry by R.C. Bauer, J.P. Birk, and D.J. Sawyer.

In this type of "line notation", the components at the site of oxidation (the anode) are listed on the left; at the site of reduction (the cathode), on the right; and central double vertical lines represent the salt bridge. A single vertical line indicates a phase difference.

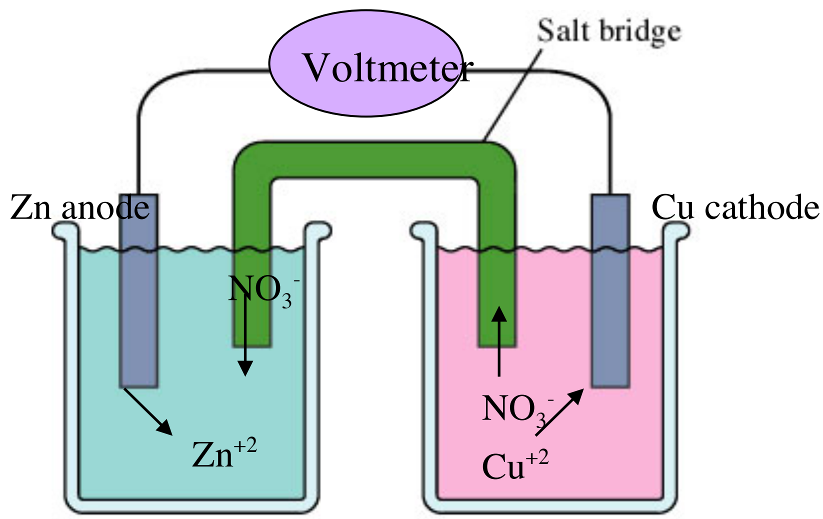

Figure 1. Functional galvanic cell based on oxidation of Zn and reduction of Cu^{+2}.

Electrons that are generated at the anode of an electrochemical cell are driven toward the cathode by a thermodynamic tendency called the *electromotive force* (emf), measured in volts. The emf is also called the *cell potential* and depends on both the identities of the substances involved in the redox reactions as well as their concentrations. By convention, the standard cell potential E^o_{cell} corresponds to cell voltages under standard state conditions- gases at 1 atm pressure, solutions at 1 M concentrations, and temperatures at 25ºC.

The overall cell potential can be regarded as the sum of the two half-cell potentials:

$$E_{cell} = E_{cathode} - E_{anode} \qquad (1)$$

Half-cell potentials are assigned relative to a reference, the standard hydrogen half-reaction that by convention has a standard reduction potential of exactly 0.000 Volts:

$$2\ H^+\ (1\ M) + 2\ e^- \text{ --> } H_2\ (1\ atm) \qquad E^o_{red} = 0.000\ V$$

Thus, creation of a voltaic cell that has the following half-reactions allows calculation of the E_{ox} of Zn via the measured E^o_{cell}:

$$Zn\ (s) \text{ --> } Zn^{+2}\ (aq) + 2\ e^- \qquad E^o_{anode} = ?$$

$$2\ H^+\ (1\ M) + 2\ e^- \text{ --> } H_2\ (1\ atm) \qquad E^o_{cathode} = 0.000\ V$$

$$\text{net rxn: } Zn\ (s) + 2\ H^+\ (aq) \text{ --> } H_2\ (g) + Zn^{+2}\ (aq) \qquad E^o_{cell} = 0.76\ V$$

Equation (1) above allows calculation of the standard reduction potential of Zn as follows:

$$E_{cell} = 0.76\ V = E_{cathode} - E_{anode} = 0\ V - (E_{anode})$$

Note that by convention, half-cell potentials are listed as reductions. Thus,

$$Zn^{+2}\ (aq) + 2\ e^{-} \text{ --> } Zn\ (s) \qquad E^{o}_{red} = -0.76\ V$$

By measuring other standard-cell emf values containing the standard hydrogen half-reaction, we can establish a series of standard potentials for other half-reactions.

Cell potentials for product-favored electrochemical reactions are positive. The exact relationship between the Gibbs free energy and the cell potential is as follows:

$$\Delta G^{o}_{rxn} = -nFE^{o} \qquad (2)$$

where n is the number of electrons transferred in the balanced redox reaction and F is the Faraday constant (96,500 J/V-mol), the charge on a mole of electrons. Thus, to achieve a favorable free energy change (a negative value), the cell potential must be positive.

Your mission in this experiment is three-fold: you will construct three electrochemical cells from unknown chemical components and measure their cell potentials. You will infer the identity of one of the metals from its physical characteristics and use its literature value for the reduction potential in combination with the measured cell potentials to calculate the unknown half-cell potentials (thus determining the identities of the unknown metals) and the equilibrium constants for the reactions. You will then measure the cell potential of one of your galvanic cells as a function of temperature, allowing determination of the thermodynamic constants ΔG, ΔH, and ΔS for the redox reaction via the following relationship:

$$\Delta G = \Delta H - T\Delta S \qquad (7)$$

ΔG can be determined from the cell potential ala equation (2) and the other two parameters can be obtained graphically by plotting ΔG versus T. Finally, you will attempt to create the best battery possible from the few raw materials that the castaways may have on the island: a pocket full of coins, some citrus fruit, and some scraps of metal salvaged from the shipwreck. The battery may be used to power up your short-wave radio so that you can call for help, which would certainly make you the most useful member of the cast.

Pre-Interview Assignments

Week 1 Due Friday, April 13th before 9am

Your regularly scheduled lab time will be your interview time. Outline Part I and II of the provided procedure (into your lab notebook), prior to your interview time and answer the following questions. Show all work and print the graph needed to answer the 2nd question:

1. For the voltaic cell Fe | Fe^{+2} (1 M) || Cu^{+2} (1 M) | Cu calculate the standard cell potential. Is this reaction favorable as written?

2. For the following voltaic cell Pb | Pb^{+2} (1 M) || Cu^{+2} (1 M) | Cu
   for which the following data were obtained, determine Δ*G* at each temperature, then graph Δ*G* versus absolute T. Find the Δ*H* value for this battery and the Δ*S* value using the graph created. Note that while there can be several values for Δ*G* there is just one value for Δ*H* and only one value for Δ*S*.

Measured Cell Potential (V)	Temperature (°C)
0.464	25
0.468	35
0.473	45

Week 2 Due upon your prompt arrival to the 2nd interview

1. No procedure outline.
2. At least one fruit or juice.
3. Coins

Experimental Procedure for Week 1 Professor Interview

Part I. Construct an Electrochemical Cell

You will be provided with three unidentified metals labeled M_1, M_2, and M_3 and three metal ion solutions, containing 1.0 M solutions of the corresponding metal-nitrate solutions [$M_1(NO_3)_?$, $M_2(NO_3)_?$, and $M_3(NO_3)_?$]. Note that one of the metals is distinctly different in appearance from the others and should identifiable based on its physical properties. This metal will make a useful reference in identifying the other metals.

1. You are provided 30 mL of 1.0 M $M_1(NO_3)_?$, 1.0 M $M_2(NO_3)_?$, and $M_3(NO_3)_?$ in separate 50mL test tubes.

2. You are provided with metal strips of M_1, M_2 , M_3

3. Measure approximately 1 gram of agar. Pour agar into a 250 mL beaker with 100 mL of 0.1 M KNO_3. Heat and stir until agar dissolves. Keep this solution stirring. Use solution to fill tubing to create salt bridges. The syringe is useful for filling the tubing. The cotton balls are necessary plugs for each end of the salt bridge. This should be enough agar to pour three salt bridges, one for each of the designated electrochemical cells.

4. Invert a U-tube and fill it with the agar solution (via a syringe) before liquid cools. Insert cotton plugs into each end, leaving some cotton protruding from each end. Make sure that you have no gaps or big bubbles, which would seriously impede current flow. Keep cotton plugs in. Let salt bridge gel by placing it into a large beaker (to keep U shape).

5. Use a U-tube as a salt-bridge to link the two half cells provided.

6. Insert the metal M_1 strip into the tube of $M_1(NO_3)_?$ and the metal M_2 strip into the tube of $M_2(NO_3)_?$. Obtain a voltmeter and attach the positive lead (cathode) to one metal and the negative lead (anode) to the other metal.

7. Read and record the voltage and the temperature of the galvanic cell. If the voltage is negative, reverse the connection. Label a quick sketch of the battery to record which metal acted as the anode and which acted as the cathode. Do not remove the salt bridge. Disconnect meter from galvanic cell.

8. Construct the following batteries and repeat same steps completed for previous battery:

$$M_2 \mid M_2^{+?}\ (1M) \mid\mid M_3^{+?}\ (1\ M) \mid M_3$$

$$M_1 \mid M_1^{+?}\ (1M) \mid\mid M_3^{+?}\ (1\ M) \mid M_3$$

Data Analysis:

- Use the literature value for the reduction potential of the pre-identified metal to calculate the reduction potentials for the unknown half-cells at room temperature. Do these values agree between the different galvanic cells? Which galvanic cell is the most powerful? What dictates the power of a galvanic cell? Summarize your findings for each of the cells with the proper line notation.

- From the reduction potentials of the unknown metals, propose the identity of each. If one of your reduction potentials is very close to two literature values, you may wish to list *both* metals as possibilities.

- Calculate ΔG for each of the 3 batteries.

- Calculate equilibrium constant for the three reactions at measured temperature.

Part II. Effect of Temperature on Cell Potential

1. Pick the electrochemical cell with the largest cell potential of the three that were measured. Now measure the cell potential of that battery as a function of temperature. Place chosen galvanic cell into an 800-mL beaker that contains enough deionized water to cover the bottom of each tube as much as possible.

2. Begin heating the water in the beaker on the hot plate, making sure that the test tubes are firmly clamped into place. DO NOT MOVE ANY PART OF YOUR GALVANIC CELL or the battery voltage will fluctuate.

3. While this battery is heating, clean up the other two batteries by removing metal strips. Wash each strip and wipe dry with paper towel. Remove salt bridges and squeeze into trash. Flush warm water through each tube to clean. Wash syringe with warm water and a brush to knock gel off. Re-cap each half cell of metal solution.

4. Heat the cell to approximately 70ºC. Measure and record the temperature and the cell potential.

5. Turn off the hot plate and record the temperature and cell potential at 10ºC intervals as the cell cools back down to room temperature (around 20 °C).

6. Carefully replace the beaker with another beaker containing an ice-water mixture without moving the test tubes. After the cell has sufficiently cooled down (around 0 °C), measure and record the temperature and the cell potential.

7. Once your data is graphed, clean up remaining battery (as directed in step 3 above).

Data Analysis

- Calculate the ΔG for this battery at each temperature. Plot ΔG versus temperature and use this plot to determine the ΔS and the ΔH for this reaction.

Experimental Procedure for Week 2 Professor Interview

Part III. Construction of a Battery from Sundry Items

In 1800 Alessandro Volta created the first battery, consisting of alternating layers of zinc, paper soaked in salt water, and silver. You will attempt to do this with coins. You will also attempt to make a battery from citrus fruits (or fruit juice) with copper and magnesium electrodes.

A. Spend no more than 1 hour on the following tasks.

1. Prepare a saturated solution of NaCl for soaking the provided filter paper.

2. Alternate layers of pennies, paper soaked in salt water, and dimes and/or nickels and/or quarters. Assemble your pile with rubber bands or Teflon-coated clamps. You may need to clean your coins first with acetic acid. Measure the voltage of the pile using provided resources.

3. Design experiments to address the following questions:
   - Does the voltage vary with the height of the coin pile?
   - Does voltage vary consistently with additional layers?
   - Does the voltage vary with different concentrations of salt water?
     How can you account for this on a desert island?
   - How does the voltage vary with different types of coins?
   - How does the voltage vary with different coin arrangements?
   - Can you increase the output of your battery by hooking up several piles of coins in series?

B. You have until end of assigned interview time to complete the following tasks:

Create a battery by connecting citrus fruits (or juice) with electrical leads via electrodes of magnesium ribbon and copper wire. The copper is a passive electrode for the reduction of H^+ to H_2 in the fruit juice (does this make copper the anode or the cathode?). You may also wish to hook up more than one of these batteries in series (i.e., copper electrode to magnesium electrode, which should increase the total available *voltage*) and/or in parallel (i.e., copper electrode to copper electrode, which should increase the total available *current*). Keep in mind that although voltage is independent of the amount of material (i.e., juice), the current increases with more material. Remember that your ultimate goal is to produce sufficient voltage *and* current to power the short-wave radio, which would require 6 volts, so you should consider how you would achieve this with your set-up.

1. When you are confident that you have created the best battery possible, you will need to demonstrate to your interviewer that your battery powers one 2.1 volt device, such as a mini-buzzer that will start buzzing when sufficiently powered.
2. You will also need to demonstrate to your interviewer that your battery can power a 1.5 volt device, such as a light-emitting diode, LED. With the LED, the long lead should go to the copper electrode and the short lead to the magnesium electrode. If you reverse this direction, you will short out the LED.

As you attempt to hook up one of these devices, there are some additional points to consider:

- voltage (the *potential* for electrons to flow) is not the only important factor in powering an external device; the current (actual electron flow) is also crucial.
- current is affected by the *amount* of material in your battery.
- voltage = current * resistance, so the more resistance in your circuit, the less current will flow. If you're having trouble powering your device despite sufficient voltage, you probably have too much resistance and therefore not enough current.

Report

Submit a one-page typed letter to the producers of *Survival Island* describing and *explaining* your findings. How would you use these findings to help the castaways if you were selected as the Professor? You should attach any graphs or tables that you feel are necessary to validate your claims. No one can help you write this letter- this is YOU trying to get a job based on your own expertise, knowledge, and merits. You decide what is important to present and how to best present facts you've obtained, objectively. Let your creativity shine!