Experiment 11

ELECTROCHEMICAL CELLS

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PURPOSE

You will construct a series of electrochemical cells. For each cell, you will measure the voltage and compare it with the calculated standard value. You will learn about the accuracy of electrochemical measurements. You will practice writing simple redox reactions and calculating ΔG and $\Delta G°$ for these reactions.

CELL CONSTRUCTION AND POTENTIALS

In principle, any spontaneous redox (oxidation-reduction) reaction can be used to construct an electrochemical cell. See Figure 1.

First, it is necessary to physically separate the chemicals involved in the oxidation and reduction half-reactions. We will place aqueous solutions of two different metal salts in separate beakers. Then, metal electrodes are added. The oxidation and reduction electrodes are commonly referred to as the **anode** and **cathode**, respectively. These terms derive from the fact that, when a voltaic cell reaction is running, anions migrate to the anode (to cast off their electrons and make it negative), and cations migrate to the cathode (to grab some electrons and leave it positive).

Next, wires are used to connect the electrodes with a voltmeter inserted to measure the cell potential. When using a cell to power an electrical device (motor, light bulb, …), the device would be inserted in place of the voltmeter.
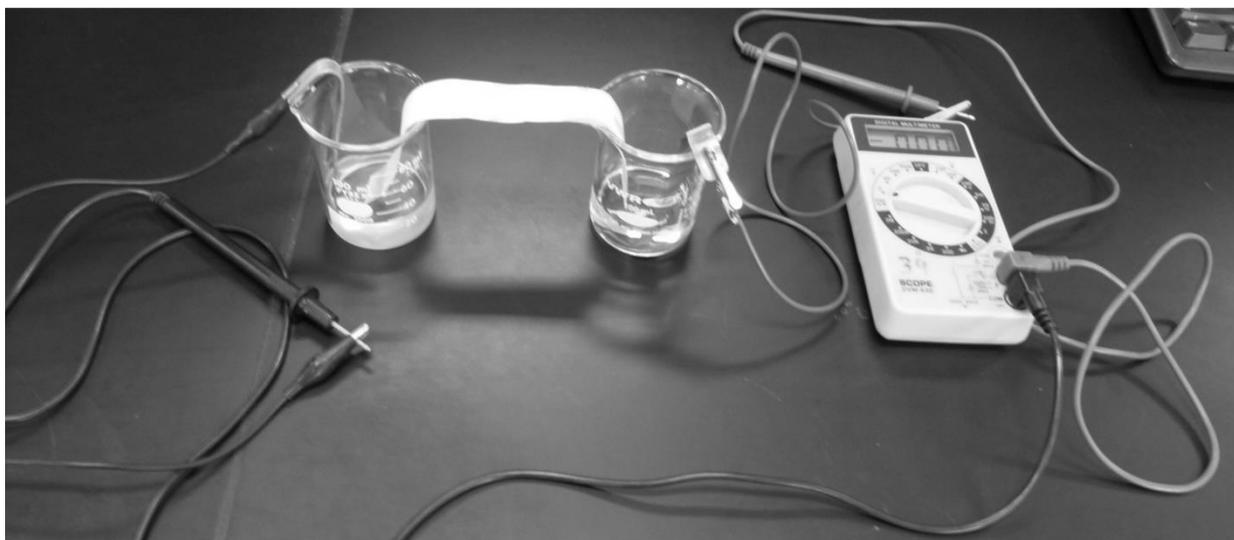

Figure 1. A sample setup for construction and voltage measurement of electrochemical cells. (Please do <u>not</u> bend the metal electrodes the way they are shown in the figure.)

Finally, provision must be made for ions to flow between the half-cells, to complete the "internal" circuit but yet not allow the reactants to mix. A **salt bridge** composed of an absorptive material impregnated with an inert electrolyte is commonly used. A strip of filter paper soaked in 0.10 M KNO_3 makes a surprisingly adequate salt bridge.

The voltage of a cell (E_{cell}) is related to the potential energy difference between electrons at the two electrodes, in units of joules/coulomb. This can be thought of as the difference between the two half-cell potentials.

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

While reduction occurs at the cathode, oxidation occurs at the anode. By convention, it was chosen to use reduction potentials for both half-cells. Since oxidation is the opposite of reduction, an oxidation potential is equal in magnitude, but opposite in sign, to the corresponding reduction potential. So, this is why the *reduction* potential corresponding to the *anode* half-reaction must be *subtracted* in equation (1a).
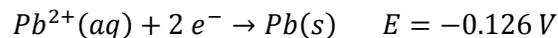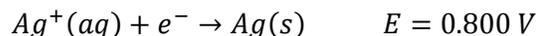
HALF-CELL REDUCTION POTENTIALS

The voltage that we measure is related to the difference in potential energy between the two half-cells. Thus, we cannot measure the potential of a single half-cell by itself. By standard convention, the reduction potential of the standard hydrogen electrode, SHE, is chosen to be 0.00 V and all other values are measured relative to it

$$2\,H^+(aq, 1\,M) + 2\,e^- \rightarrow H_2(g, 1\,bar) \qquad (2)$$
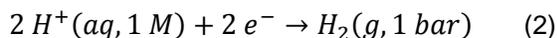
So, for example, when a SHE is connected to a half-cell containing $Ag^+|Ag$, the silver electrode is found to be the positive electrode (meaning it is the cathode and that it is easier to reduce the Ag^+ than the H^+) and the measured cell potential is 0.800 V. Therefore, the $Ag^+|Ag$ half-cell is assigned a reduction potential of 0.800 V.
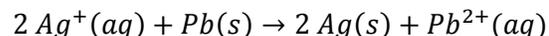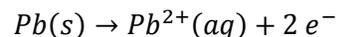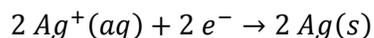
Similarly, when the SHE is connected to a $Pb^{2+}|Pb$ half-cell, the SHE is found to be the positive electrode (so it is easier to reduce the H^+ than the Pb^{2+}) and the measured cell potential is 0.126 V. So, the $Pb^{2+}|Pb$ electrode is assigned a reduction potential of -0.126 V.

We can use the half-cell reduction potentials to predict the cell potential for a Ag || Pb cell.

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E = 0.800\,V$$
$$Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s) \qquad E = -0.126\,V$$

Since the $Ag^+|Ag$ half-cell has the greater reduction potential, the Ag^+ will be reduced at the cathode and the Pb will be oxidized at the anode and $E_{cell} = 0.800\,V - -0.126\,V = 0.926\,V$, using equation 1(a).

The complete cell reaction can now be obtained by reversing the Pb half-cell reaction (since the Pb is oxidized) and then adding the two half-reactions together. However, since the number of electrons must cancel, we need to multiply the Ag half-cell reaction by 2 to yield:

$$2\,Ag^+(aq) + 2\,e^- \rightarrow 2\,Ag(s)$$
$$Pb(s) \rightarrow Pb^{2+}(aq) + 2\,e^-$$
_____
$$2\,Ag^+(aq) + Pb(s) \rightarrow 2\,Ag(s) + Pb^{2+}(aq)$$

When the concentrations of all ions present are exactly 1 M (standard conditions), the result is the standard cell potential

$$E^O_{cell} = E^O_{cathode} - E^O_{anode} \qquad (1b)$$

where E^O for each half-cell may be obtained from a table of standard reduction potentials.

VOLTAGE AND ΔG

The voltage is also related to the Gibbs free energy of the chemical reaction

$$\Delta G = -nFE \qquad (3a)$$

where n is the number of electrons transferred in the balanced equation (n=2 in the Ag || Pb cell), E is the cell's voltage, and F is the Faraday constant (96.5 kJ V^{-1} mol^{-1}, using convenient units). If the cell is a standard cell, then

$$\Delta G° = -nFE° \qquad (3b)$$

Notice that a *negative* ΔG, which corresponds to a spontaneous reaction, results in a *positive* voltage. Thus, the direction of a reaction that will be spontaneous can be deduced by noting how the electrodes must be connected to a voltmeter to give a positive reading.
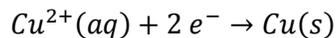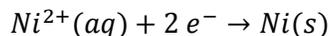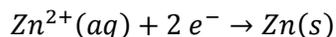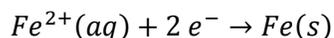
VOLTMETER READINGS

The available multimeters in lab are capable of measuring resistance, current or voltage. All three functions share one terminal in common, on our meters labeled "COM." By convention, this terminal is to be connected with *negative* polarity. The other voltage terminal, although perhaps labeled only "V," must be the "positive" or "+" terminal.

A voltmeter gives a positive reading when the positive terminal is *in fact* more positive than the common or negative terminal. Thus, we can deduce that a *negative* terminal must be connected to an electrode where electrons are being produced, i.e., where *oxidation* occurs. Similarly, a *positive* terminal must be connected to an electrode from which electrons are being removed, i.e., where *reduction* spontaneously occurs. **Therefore, a positive voltmeter reading means that the half-cell with the higher reduction potential is connected to the positive terminal.**

IN THIS EXPERIMENT

Four half-cells will be constructed and these half-cells will be combined in all six possible combinations to construct electrochemical cells. The voltage of each cell will be measured twice (at least) to ascertain the reproducibility of these measurements.

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

$$Ni^{2+}(aq) + 2\,e^- \rightarrow Ni(s)$$
$$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$$

The average measured voltage of each cell will be compared with the expected voltage calculated from the standard reduction potentials from your textbook. Note that the measured cell voltages are expected to roughly, *but not exactly*, match voltages calculated using textbook standard half-reaction $E°$ values. The latter correspond to reactions carried out in *hypothetical, ideal* standard states, which your setups are not.

We will then examine the reactions when we include an Al³⁺|Al half-cell with each of the four previously-constructed half-cells.

$$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$$
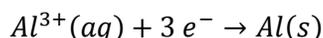
There are physical characteristics of the Al³⁺|Al half-cell that result in some interesting behavior.

Finally, you will write balanced cell reactions and then calculate ΔG and $\Delta G°$ for some of the cells that you constructed. For each cell reaction, one of these *reduction* half-reactions must be reversed to provide the *oxidation* necessary for a balanced redox reaction. Although *the molecules* will decide which half-reaction is to be reversed, you can make a good prediction by comparing the measured reduction potentials. The half-cell with the most positive reduction potential should remain as a reduction.

PRE-LABORATORY PREPARATION

1. Read the procedure and look over the Data Sheet and Data Analysis section of the experiment.

2. Complete the Prelab assignment in Canvas. Refer to the background section of this experiment, as necessary.

3. You will need to look up the standard reduction potential for each of the five half-cells used. THESE SHOULD BE FILLED IN THE TABLE AT THE START OF THE DATA ANALYSIS SECTION!

EXPERIMENTAL SECTION

REAGENTS PROVIDED

0.10 *M* solutions of KNO₃, CuSO₄, ZnSO₄, NiSO₄, and FeSO₄
0.050 M Al₂(SO₄)₃ (which is 0.10 M in Al³⁺)
Solid metal electrodes
Filter paper for construction of salt bridges

Hazardous Chemicals

NiSO₄ – possible carcinogen and poison. Do not swallow it and avoid skin contact. Wash off immediately with copious amounts of water if your skin comes in contact with it.
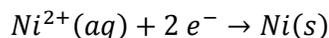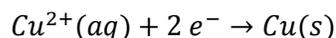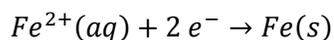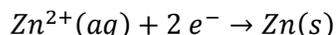

WASTE DISPOSAL

The Ni and Cu solutions should be disposed of in the designated waste containers. Other solutions may be safely washed down the sink.

PROCEDURE

This experiment will be done with a partner.

1. Construct separate half-cells for each of the four half-reactions:

$$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$$
$$Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$$
$$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$$
$$Ni^{2+}(aq) + 2\,e^- \rightarrow Ni(s)$$

(a) Add approximately 40 mL of each of the five metal salt solutions to separate 100-mL beakers. (If you do not have enough 100-mL beakers, you can use 50-mL beakers instead, in which case you should only use 30 mL of salt solution, so that the menisci of all of the solutions are at the same level).

(b) Obtain one metal electrode of each of the four metals. Note that the identity of the metal is stamped on each electrode.

(c) If necessary, very lightly sandpaper the metal electrodes to remove corrosion products and ensure good contact. This is not likely to be necessary except for possibly iron and zinc. If you sand an electrode, be sure to wipe it off with a paper towel to remove the sanding debris.

(d) Stand the clean electrode in the corresponding solution. Please do NOT bend the electrodes.

2. Add about 100 mL of 0.10*M* KNO₃(aq) to a 250 mL beaker. This bath will be used for making salt bridges.

Two groups could share a single bath.

3. Measure the voltage for <u>each of the six cells</u> you can construct by pairing the half-cells with each other:

(a) Soak a piece of filter paper in 0.10 *M* KNO₃. Pick up the strip by the middle, and drain excess solution by touching the ends to a paper towel. Position the paper-strip salt bridge so that it makes contact with both solutions, but is not touching the electrodes. See Figure 1. <u>Use a new salt bridge for every voltage measurement.</u>

(b) Connect the multimeter leads to the two electrodes and set the multimeter to the 2V scale. (On some of the voltmeters this is the 2000 mV scale. If you have one of these voltmeters, you will need to convert the mV to V.) <u>If it is negative, reverse the leads to obtain a positive voltage reading</u>.

(c) Swirl the solutions for a couple seconds, wait a couple of seconds for the reading to roughly stabilize and then <u>record it (to the nearest 0.001 V) in Data Table I. Also, circle which metal electrode was the positive one.</u>

4. After completing all six measurements, determine the technique's reproducibility by repeating each of them, using the following procedure:
(a) Remove and dry the electrodes. Resand them if necessary (it probably is not).
(b) Dispose of the two "colorless" solutions, Fe^{2+} and Zn^{2+}, down the drain and get fresh samples. However, use the same Cu^{2+} and Ni^{2+} solutions to minimize waste.
(c) Place the metal electrodes in the solutions,
(d) Repeat the six measurements using the same procedure as in step 3. Record these voltage readings. (These are the Second Voltages in Data Table I.)
(e) If the two voltage readings for the same cell differ by more than 0.1 V, get a fresh solution of Fe^{2+} and/or Zn^{2+}, if relevant, and then repeat the measurement a third time.
(f) Average your two readings (or your two closest readings if you took three readings).

5. Construct an $Al^{3+}|Al$ half-cell, following the same procedure used in step 1.

Since both Zn^{2+} and Al^{3+} are colorless, you may want to label the $Al^{3+}|Al$ half-cell.

6. Measure the voltage for <u>each of the four cells</u> you can construct by pairing the $Al^{3+}|Al$ half-cell with each of the others.

Follow the same procedure as in step 3. Record your results in Data Table II. You do NOT need to repeat these measurements.

The results you obtain may not be what you expect.

7. Re-measure the voltage for the cell constructed using the $Al^{3+}|Al$ and $Cu^{2+}|Cu$ half-cells, using the following procedure:
(a) Attach the positive lead to the copper electrode.
(b) The negative lead should not be attached to any electrode, but should be ready.
(c) Place a salt bridge, as normal, between the Al^{3+} and Cu^{2+} solutions.
(d) Remove the Al metal electrode from its solution and dry it.
The next several steps need to be done quickly.
(e) Sand the bottom on one side of the Al electrode for a few (3-5) seconds.
(f) Attach the negative lead to the Al electrode.
(g) Insert the Al electrode into the Al solution and record the very first voltage reading you see (in Data Table III). Do NOT wait for the voltage to stabilize before taking the reading,
(h) Watch the voltage reading for about one minute. Use the electrode to gently swirl the solution every 15-20 seconds. Record the final voltage reading.

8. Return the multimeter, electrodes, and wires to the front bench. <u>Be sure to turn the multimeter off.</u> Wash and store your glassware.

Wash your hands thoroughly before leaving lab.

Name _____   Station Used _____   Instructor/Day/Time _____

Partner _____   Station Checked & Approved _____

DATA SHEET AND DATA ANALYSIS

Record and calculate all values to the proper number of significant figures.   All measured *voltages* should be positive (although *half-cell reduction potentials* can be positive or negative).

STANDARD HALF-CELL REDUCTION POTENTIALS (Lookup these values in your textbook)

Half-Cell	$Cu^{2+}|Cu$	$Ni^{2+}|Ni$	$Fe^{2+}|Fe$	$Zn^{2+}|Zn$	$Al^{3+}|Al$
Standard Reduction Potential, $E°$ (V)					

DATA TABLE I. Measured Voltages for Cells Not Containing Al

Metal Electrodes	Circle the Positive Electrode	First Voltage (V)	Second Voltage (V)	Third Voltage (V) (if necessary)	Average Measured Voltage (V)	Calculated Standard Voltage, $E°$ (V)
Cu || Ni	Cu or Ni					
Cu || Fe	Cu or Fe					
Cu || Zn	Cu or Zn					
Zn || Ni	Zn or Ni					
Zn || Fe	Zn or Fe					
Ni || Fe	Ni or Fe					

1. Calculate the average measured voltage using your two closest measurements.

2. Complete the column of Calculated Standard Voltages (cell potentials) by using equation 1(b) and the standard half-cell reduction potentials that you looked up from your textbook. Show the calculation for the Cu \|\| Ni cell below.

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DATA TABLE II. Measured Voltages for Cells Containing the $Al^{3+}|Al$ Half-Cell

Metal Electrodes	Positive Electrode	Measured Voltage, E_{cell} (V)	Calculated Standard Voltage, $E°_{cell}$ (V)
Fe || Al	Fe or Al		
Zn || Al	Zn or Al		
Ni || Al	Ni or Al		
Cu || Al	Cu or Al		

3. Use equation 1(b) and the *Standard Reduction Potentials* to complete the *Calculated Standard Voltage* column of Data Table II (as in step 2, above).

4. Combine the two relevant half-reactions to write the balanced (net ionic) reaction observed in the each of the four specified cells. Hint: to determine the direction of the reaction, look at which electrode you observed to be positive (indicating this is the half-cell where reduction occurred).

Cu || Ni	
Zn || Ni	
Ni || Fe	
Cu || Al	

5. For each of the above reactions, do parts A-C and record your results in the table below:
   A. **Use the balanced (net ionic) reaction to determine n.**
   B. **Calculate ΔG using the appropriate *Measured Voltages* (from Data Tables I or II).**
   C. **Calculate $\Delta G°$ using the *Calculated Standard Voltages* (from Data Tables I or II).**

   Show a sample calculation for $\Delta G°$ for the Cu \|\| Ni reaction in the space below.

	n	Calculated ΔG (kJ/mol)	Calculated $\Delta G°$ (kJ/mol)
Cu || Ni			
Zn || Ni			
Ni || Fe			
Cu || Al			

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DATA TABLE III. Voltages at different times for the Cu || Al cell.

Previously Measured Voltage (V) (from Table II)	Initial Voltage (V)	Final Voltage (V)

6. It is known that Al metal does not corrode easily because Al metal will form a stable coating of aluminum oxide that protects the metal underneath so it will not oxidize. Given this information, answer the following questions for the Cu || Al cell:

   A. **Circle your choice from each pair:** Immediately after sanding the Al electrode, the initial voltage was (***higher / lower***) than the previously measured voltage. This means the initial voltage is (***closer to / farther from***) its standard value (see Data Table II).

   B. **Why do you think sanding the electrode would cause this change (relative to its standard value)?**

   C. **The cell voltage should have changed during the minute that you observed it. Explain what is physically occurring on the electrode that causes the voltage to change.**