Lab 9: Electrochemistry, Galvanic Cells

Background

Chemical reactions involving the transfer of electrons from one reactant to another are called *oxidation-reduction* 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). See the below oxidation and reduction reactions:

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

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

The oxidation number of Zn(s) is 0 and the oxidation number of Zn^{2+} is +2. Therefore, in that half-reaction, the oxidation number ***increases***, which is another way of defining an ***oxidation*** reaction. In contrast, the oxidation number of Cu^{2+} is +2, and the oxidation number of Cu(s) is 0. In this half-reaction, the oxidation number *decreases*, meaning that it undergoes a ***reduction*** reaction.

You will notice that in the half-reactions above, both mass and charge are balanced. This statement must be satisfied for all electrochemical half-reactions. It is also true that 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* (see below):

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad (3)$$

The electrons are not shown in this redox reaction, because they are neither products nor reactants, but have simply been transferred from Zn to Cu^{2+}.

A measure of the tendency for a reduction to occur is its ***reduction potential, E***, measured in volts. At standard conditions (25 °C and concentrations of 1.0 M), the measured voltage of the reduction half-reaction is defined as the *standard reduction potential, E^o*. Standard reduction potentials have been measured for many half-reactions. You can find these listed in your lecture textbook, Appendix D, Page A-14.

The standard reduction potentials for zinc and copper are -0.76 V and +0.34 V, respectively. The more positive the reduction potential, the greater is the tendency for the reduction to occur. Therefore, Cu^{2+} has a greater tendency to be reduced than Zn^{2+}.

Galvanic Cells

A *galvanic cell* is a device in which a redox reaction (such as the one in equation (3)), spontaneously occurs and produces an electric current. In order for the transfer of electrons in a redox reaction to produce this electrical current and be useful, the electrons are made to pass through an external wire, instead of being directly transferred between the aqueous ions. The design of a galvanic cell (shown in Figure 1) allows this to occur.

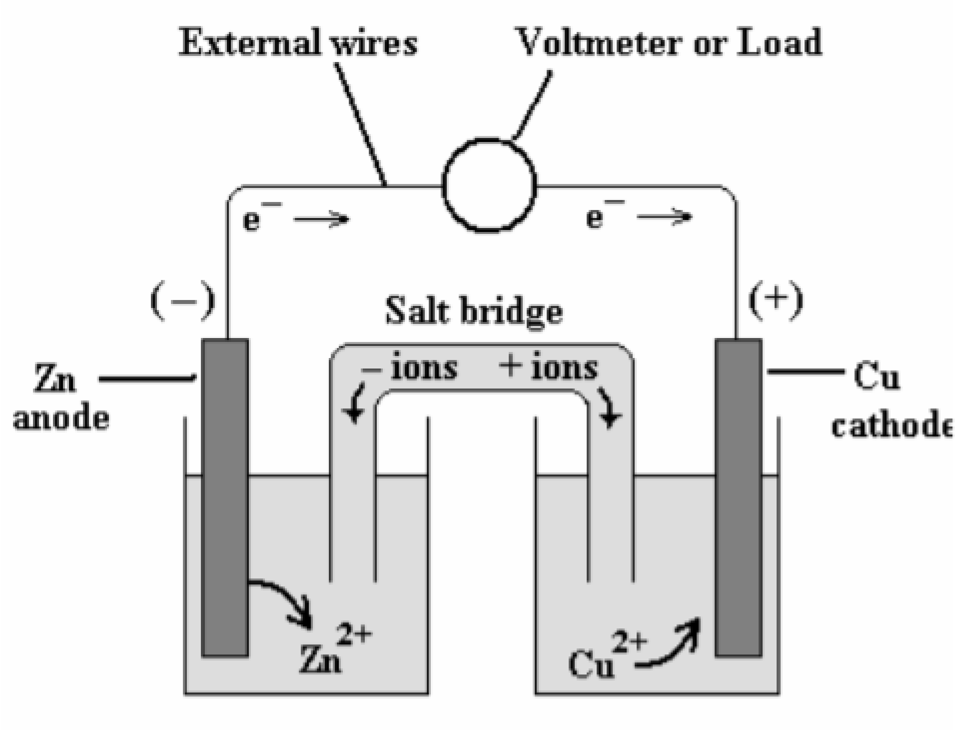

Figure 1: Galvanic cell based on the redox reaction in equation (3).

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 (called an *electrode*) is placed in the solution and connected to an external wire. The electrode at which the oxidation occurs is called the ***anode***, and the electrode at which reduction occurs is called the ***cathode***. The two half-cells are connected by a *salt bridge* that allows a “current” of ions to flow from one half-cell to the other. When the two electrodes are connected to an electric load (such as a light bulb or voltmeter) the circuit is completed, the oxidation and reduction reactions occurs, and the electrons move from the anode (-) to the cathode (+), producing an electric current.

The cell potential, E_{cell}, which is a measure of the voltage that the galvanic cell can provide, is calculated from the half-cell reduction potentials that were defined earlier:

$E_{cell} = E_{cathode} – E_{anode}$

At standard conditions, indicated by the superscript °, the *standard cell potential,* E^o_{cell}, is based upon the standard reduction potentials, as shown in equation (4)

$$E^o_{cell} = E^o_{cathode} – E^o_{anode} \qquad (4)$$

Based on the values for the standard reduction potentials for the two half-cells in equation (3), the standard cell potential, E^o_{cell}, for the galvanic cell in Figure 1 would be:

E^o_{cell} = +0.34V – (-0.76 V) = +1.10 V

The positive voltage for E^o_{cell} indicates that, at standard conditions, the reaction is *spontaneous*.

The Nernst Equation

When conditions are not standard, the ***Nernst Equation*** (equation (5)) is used to calculate the potential of a cell. It takes the standard cell potential (E^{o}_{cell}) and subtracts a correction factor from that standard potential that incorporates differences in concentration or temperature that are not standard (RT/nflnQ)

$$E_{cell} = E^{0}{}_{cell} - \frac{RT}{nF}\ln Q \qquad (5)$$

In the Nernst Equation, R is the universal gas constant (8.314 J/Kmol), T is temperature in Kelvin, and n is the number of electrons transferred in the redox reaction (e.g. n = 2 in equation (3)). F is the Faraday constant (96,485 J/Vmol).

Finally, recall that Q is the reaction quotient for the ion products/ion reactants of the cell (this was touched upon during past equilibrium discussions). The solid electrodes have constant "concentrations" and so do not appear in Q. See the below example:

Example:

For our equation (3) example, $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, so Q is equal to:

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

as this is products divided by reactants (remember that solids are not included in reaction quotients). This leads to lnQ being equal to:

$$lnQ = \ln[Zn^{2+}] - \ln\,[Cu^{2+}]$$

Since in equation (3), n = 2, the Nernst equation for this redox reaction becomes:

$$E_{cell} = E^{0}{}_{cell} - \frac{RT}{2F}\ln[Zn^{2+}] + \frac{RT}{2F}\ln\,[Cu^{2+}] \qquad (6)$$

The Experiment

Part A: Reduction Potentials

You will construct a series of galvanic cells, making all possible combinations of the different metal half-reactions (Cu, Fe, and Zn). You will measure the cell potentials, E^{o}_{cell}, using a Vernier voltage probe, as shown in Figure 3. You will use the 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^{o}_{cell}, as evident from the Nernst Equation (5).

Part B: Nernst Equation for Varying Zn^{2+} Concentrations

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

Calculations for Part B: Example

If you were to perform a series of experiments in which [Zn^{2+}] is kept constant while [Cu^{2+}] is varied, E_{cell} can be measured and it will be found to vary with ln[Cu^{2+}]. A plot of the data obtained in which y is E_{cell} and x is ln[Cu^{2+}] will result in a straight line (y = mx +b). For equation (6), both of the terms E^o_{cell} and –[RT/2F]ln[Zn^{2+}] are constant and together equal the intercept, b, of the line. [RT/2F] will be the constant slope, m, provided that the temperature is constant.

Thus, a plot such as the one shown in Figure 2 can be generated by measuring the cell potential for different values of [Cu^{2+}], while keeping [Zn^{2+}] constant. The equation of the line can then be used to determine ln[Cu^{2}] in a solution of unknown concentration for its measured E_{cell}, as long as standard conditions are met. This is the same principle used in Lab 2, when performing the UV-Vis analysis. Notice that as the concentration of Cu^{2+} ion reactant increases, the potential of the cell increases.

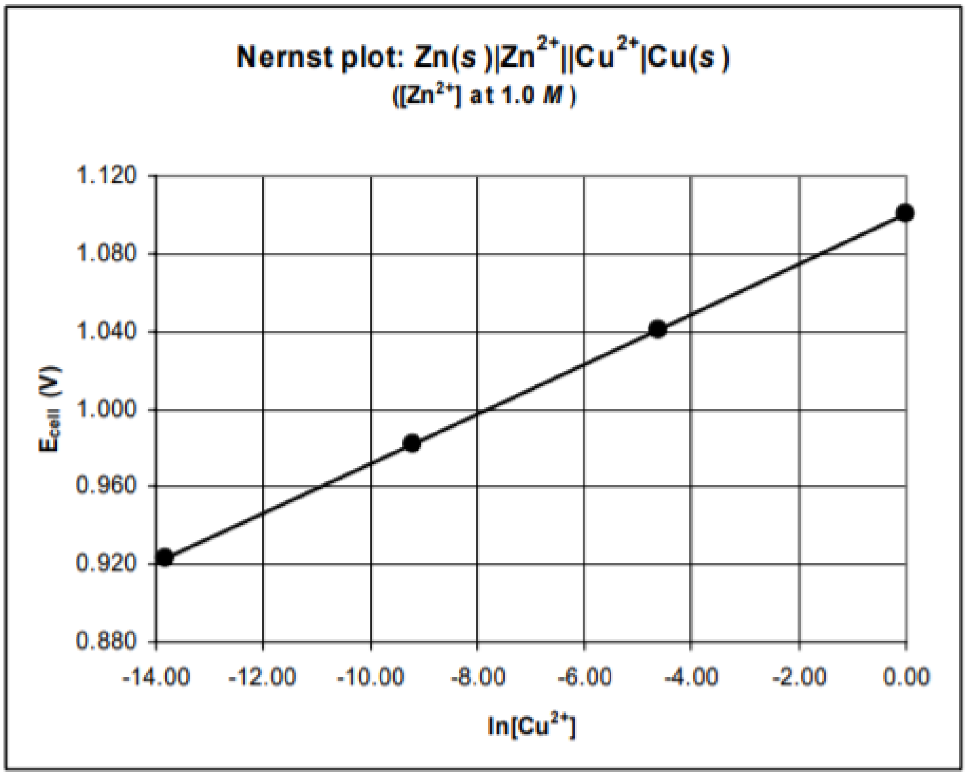

Figure 2: Nernst plot of E_{cell} vs ln[Cu^{2+}] ([Zn^{2+}] constant at 1.0 M).

Procedure

Part A

1) Wet a 2-3 inch-long strip of filter paper with NaCl solution. Remove excess liquid *gently* by blotting it with a paper towel and fold the paper into a U-shape; this will serve as your salt bridge

2) 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).

3) 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 well. Do not immerse the copper and zinc electrodes at this time!

4) 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! Make sure to note which was which in your lab notebook!**

5) Immerse the electrodes in the solutions, making sure to avoid contact with the salt bridge. Take the potential reading when the voltage has stabilized. If the voltage reading on the Vernier is positive, the electrodes are connected correctly; if not repolish and rinse the electrodes, then reverse the connections.

6) Record the positive cell potential, in volts, in your lab notebook.

a) Note: You will find that the voltage recorded is less than what you would expect based on standard reduction potentials. 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 all above steps for galvanic cells of **Fe (in 1.0 M $FeSO_4$) – Zn** and **Fe – Cu.** Use a freshly prepared filter paper strip for the salt bridge of each cell!

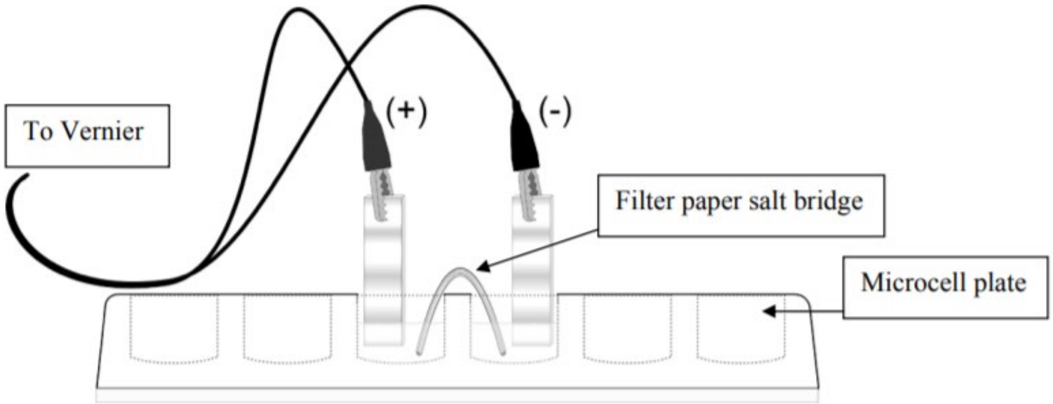

Figure 3: Galvanic cell apparatus for Part A.

Part B

1) Remove the copper and zinc electrodes form the half-cells used previously and clean and repolish them.
2) Place Solutions A, B, and C in adjacent cells to the 1.0 M $Cu(NO_3)_2$ cell. A recommended orientation would perhaps look like this:

	1M Zn (D)	0.01 M Zn (C)
1M Fe	1M Cu	0.0001M Zn (B)
	Unknown Zn	0.000001M Zn (A)

3) Connect the copper and solution A half-cell with a freshly prepared salt bridge. Connect the copper and zinc electrodes to the correct voltage probe leads.
4) Measure and record the cell potential in your lab notebook, using the same technique as described in Part A.
5) Repeat the measurement of E_{cell} (steps 3-4) for solutions B and C (**Make sure to take these measurements in this order – from lower concentration to higher concentration)**.
6) Then, in the same way, measure the E_{cell} for the unknown Zn^{2+} solution. Record the measured values in your lab notebook.

Report Sheet

Please ensure that you document all of the values in **black** on your lab notebook page! These are numbers that you will enter into LabFlow's Data Report Sheet, and will be used to calculate the values in **red.**

Part A:

Galvanic Cell	Cu - Zn	Fe - Zn	Cu - Fe
E_{cell}, Volts			
Cathode (Red lead)			
Anode (Black lead)			
Cathode potential			
Anode potential			

Part B:

Solution:	Zn^{2+} (M)	ln $[Zn^{2+}]$	Measured Potential, Volts
A	0.000001		
B	0.0001		
C	0.01		
D	1.0		

Graph of ln$[Zn^{2+}]$ vs Measured Potential (from Excel)

Best Fit Line Equation

Unknown Zinc Solution Measured Potential	
Unknown Zinc Concentration	