Electrochemical Cells

PURPOSE

To see how changes in concentration and pH affect the potential in an electrochemical cell, and confirm the Nernst equation.

GOALS

- To examine how standard reduction potentials are measured.
- To relate concentration changes to changes in cell potential.

INTRODUCTION

A galvanic cell is an electrochemical cell in which the spontaneous electrochemical reaction proceeds, that is, ΔG for the reaction is negative. The free energy decrease for a galvanic cell is proportional to the cell potential. The greater the driving force of the reaction, the greater the cell potential. The relationship is shown below.

$$\Delta G = -nFE_{\text{cell}} \tag{1}$$

where n = the number of moles of electrons passed, F is the Faraday constant (9.65×10^4 Coulombs/mole of electrons) and E_{cell} is the cell potential.

E_{cell} is positive for spontaneous reactions; electrons flow toward the more positive potential. This causes some confusion, because free energy decreases (has a negative sign) for spontaneous processes. If you remember that electrons flow toward positive charges, it is easy to keep track of this.

One can determine the standard potential of any electrochemical cell by:

1 Identifying the oxidation (anode) and reduction (cathode) half-cells.

2 Looking up the standard half-cell potentials in a table of reduction potentials. An abbreviated table is included at the end of this lab procedure. *Reminder: all potentials are listed in the table as reduction potentials.*

3 Substituting the half-cell potentials into the following equation:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}. \tag{2}$$

Standard potentials are determined at standard conditions (1 M solutions or 1 atm pressure). Although there is no standard temperature, the tables in this course are all at 25°C.

Most often, cells are not at standard conditions, and they change as the reaction proceeds. Nernst proposed that a galvanic cell would spontaneously discharge (behave like a battery) until it reaches equilibrium. Stated in another fashion, a dead battery is one in which the free energy (ΔG) is zero. For this to occur, the overall potential of the cell must decrease as the concentration of reactants decreases. The Nernst equation relates the cell potential to concentrations of reactants via the reaction coefficient, Q.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q \tag{3}$$

where R is the gas constant (8.314 J/(mol $\cdot$ K)), T is the temperature (K), and n, F and E_{cell} are as defined in equation 1 and E°_{cell} is the cell potential at standard conditions. Q is defined as the [products]$^{\text{coeff}}$ / [reactants]$^{\text{coeff}}$. Similar to K, the equilibrium constant, Q, only includes terms in the aqueous or gaseous state. An example redox reaction and the reaction quotient are given below.

$$2\ \text{Ag}^{+}(aq) + \text{Mn}(s) \rightleftharpoons 2\ \text{Ag}(s) + \text{Mn}^{2+}(aq) \qquad Q = [\text{Mn}^{2+}]/[\text{Ag}^{+}]^2$$

At 25°C and converting to log base 10, the Nernst equation becomes:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q. \tag{4}$$

Using the Nernst equation, cell potentials can be calculated from standard cell potentials and known concentrations.

According to the Nernst equation, any change to the cell that increases Q decreases E_{cell}, while any change that decreases Q will increase E_{cell}. Thus, adding reactant or removing product increases E_{cell}. Removing reactant or adding product, which is what the reaction is doing as it proceeds, decreases E_{cell}. The most general statement of the Nernst equation is that anything that makes ΔG more negative will increase E_{cell}.

In this experiment, you will measure cell potentials using the Zn/Zn^{2+} half-cell as a reference. You will use the Nernst equation to predict the dependence of cell potential on the concentration of test solutions, and verify the predictions with measurements.

In the last part of this experiment, you will measure the potential of a bioorganic half-cell and then predict and verify the dependence of cell potential on the pH with the Nernst equation. Redox reactions are ubiquitous in biological systems. Vitamin C (ascorbic acid) has been hailed as an "anti-oxidant," which simply means that it is a reducing agent. The ascorbic acid half reaction, *written as a reduction*, is shown below:

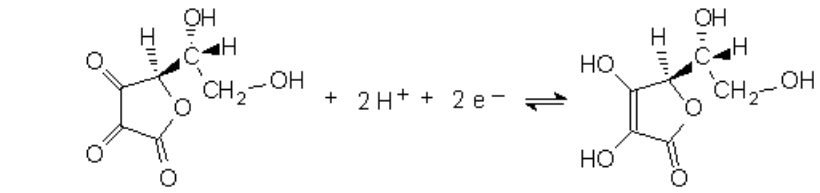

Figure 1

When ascorbic acid acts as a reducing agent, the reverse reaction occurs. Notice that H^+ participates in the half-reaction. Therefore, the concentration of H^+ (and thus the pH) will affect the reduction potential. The standard potential is defined where $[H^+] = 1\ M$, or at pH = 0. Clearly, potentials measured at biologically relevant pH's are not standard potentials.

The dependence of the reduction potential on pH is complicated because ascorbic acid is a weak diprotic acid and is singly or doubly deprotonated depending on pH. K_a for the first dissociation is 5×10^{-5}. There may be one or two protons in the half reaction, which complicates the exact calculation of the potential shift. Nonetheless, the qualitative dependence of potential on pH can be predicted from the Nernst equation.

At this point, it is worth mentioning a point about measuring potentials with a voltmeter, as you will be doing in this experiment. Most voltmeters are sensitive to the direction in which current flows, and register this as the sign of the potential. In this lab, all the reactions are spontaneous, so all the voltage measurements should have a positive sign. You will be instructed to set up your voltmeter so this is true in the first measurement, then reverse the leads and record the result, then explain what happened. Think about your response to this question now, before the lab.

In this experiment, you will measure the potential difference between a Zn^{2+}/Zn couple and Cu^{2+}/Cu, Pb^{2+}/Pb, and Ag^+/Ag couples. You will vary the concentrations of the ions in solution and measure the changes in cell potential that occur. Finally, you will measure the potential of solutions of ascorbic acid versus a Cu^{2+}/Cu couple at different pH's.

EQUIPMENT

1 MicroLab interface

1 voltmeter alligator clip leads

1 400 mL beaker for rinsings

1 100 mL beaker

1 salt bridge assembly

1 hand-held pH meter

1 deionized water squirt bottle

1 eye dropper

REAGENTS

100 mL 0.1 *M* $Zn(NO_3)_2$ (in covered plastic container)

100 mL 0.1 *M* $Cu(NO_3)_2$ (in covered plastic container)

100 mL 0.1 *M* $AgNO_3$ (in covered plastic container)

100 mL 0.1 *M* $Pb(NO_3)_2$ (in covered plastic container)

∼3" zinc wire

∼3" copper wire

∼3" silver wire

∼3" lead wire

1 graphite rod

∼1.5 mL 0.1 *M* $Cu(NO_3)_2$

∼3.0 mL 1.5 *M* KOH

solid $Na_2HPO_4 \cdot 7\ H_2O$

solid ascorbic acid

∼20 drops 3.0 *M* HCl

∼20 drops 3.0 *M* NaOH

SAFETY

3 M HCl solution gives off highly irritating vapors. Do not inhale them. Work with concentrated solutions under the hood so vapors do not build up in the lab. If you do inhale enough vapor to have a problem, move to fresh air. Have your lab partner notify your instructor about the accident.

HCl, NaOH, and KOH solutions are corrosive. They can attack the skin and cause permanent damage to the eyes. If the solution splashes into your eyes, use the eyewash immediately. Hold your eyes open and flush with water. If contact with skin or clothing occurs, flush the affected area with water. Have your lab partner notify your instructor about the spill.

Cu^{2+}, Pb^{2+}, and Ag^{+} ions are listed as toxic. If contact with skin or clothing occurs, the affected area should immediately be flushed with water. If Ag^{+} solutions contact the skin, they will produce brown spots that appear about 24 hours after exposure. They are harmless and will fade in a few days.

WASTE DISPOSAL

Test solutions that are provided in plastic containers in which measurements are to be made should *not* be discarded. When you are finished, close the containers with the proper lids and return them to the set-up area.

You will rinse the salt bridge between measurements. The rinsings can be flushed down the sink. You should label a beaker as a rinse container and use it during the experiment, and empty it when you are finished.

Diluted Cu^{2+} solution and any solid that forms in Part B should be put in the container labeled "Copper Waste."

The ascorbic acid solution can be flushed down the sink with water.

PRIOR TO CLASS

Please read the following section of Lab Safety and Practices:

- Good Lab Practices[1]

LAB PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

Part A: Measurement of Initial Cell Potentials

1 Open the MicroLab program. Make sure the alligator clip leads are connected to the interface.

2 Calibrate the mV probe as described in the MicroLab instructions provided in the lab. Note that the mV probe is factory calibrated, so you do not have to calibrate it yourself. However, to test the calibration of the mV probe, you can take a measurement with the leads connected to each other. This should give you a reading of ∼0 mV.

3 Then configure the MicroLab program to collect data using the instructions provided in the lab. Record the mV value displayed on the screen for each measurement in your lab manual.

4 Label a 400 mL beaker as a rinse container.

5 Open the containers of Zn^{2+} and Ag^{+} solution. Put the lids where they will stay clean, and you can find them again.

6 Remove the salt bridge, with lids, from the containers of KNO_3 solution.

7 If the solution in the salt bridge is low (not across the bridge) add KNO_3 solution from the plastic container.

8 Rinse the salt bridge with deionized water (into the labeled waste beaker) and blot dry.

9 Immerse the salt bridge in the Zn^{2+} and Ag^{+} solutions, one leg in each, as shown in Figure 2.

[1] ../practices/manual.html

Figure 2: Electrochemical Cell Setup

10 Use the alligator clip on the black lead to pick up the zinc wire and place it in the Zn^{2+} solution. The wire should *not* be completely submerged.

11 Use the alligator clip on the red lead to pick up the silver wire and place it in the Ag^{+} solution. The wire should *not* be completely submerged.

12 Read the voltage. If the value is negative, reverse the leads. Record the voltage in Table A.

13 Reverse the leads on the metal wires. Measure the voltage and enter it in Table A.

14 Using the alligator clip, replace the silver wire in the labeled test tube.

15 Remove the salt bridge from the solutions. Rinse it with deionized water (into the labeled waste beaker) and blot dry.

16 Replace the lid on the Ag^{+} solution and set it aside.

17 Open the container of Pb^{2+} solution and put its lid where it will stay clean.

18 Immerse the salt bridge in the Zn^{2+} and Pb^{2+} solutions, one leg in each, as shown in Figure 2.

19 Replace the black lead on the Zn wire. Use the alligator clip on the red lead to pick up the lead wire and place it in the Pb^{2+} solution. The wire should *not* be completely submerged. Record the voltage in Table A.

20 Repeat the procedure for the Cu^{2+}/Cu couple.

Part B: Dependence of Cell Potential on [Cu^{2+}]

1 Combine an eyedropper full of 0.1 *M* Cu^{2+} solution with about 60 mL of deionized water in a 100 mL beaker.

2 Measure the potential of the diluted Cu^{2+} solution versus the Zn^{2+}/Zn couple and record in Table B.

3 Add two eyedroppers full of 1.5 *M* KOH to the diluted Cu^{2+} solution, gently swirl the mixture, and observe the reaction.

4 Allow any solid that may have formed to settle to the bottom of the beaker, then measure the potential of the solution versus the Zn^{2+}/Zn couple. Record this value in Table B.

5 Dispose of the diluted Cu^{2+} solution in the waste container located on the side shelf. Rinse with deionized water from your squirt bottle and add the rinsings to the waste bottle.

Part C: pH Dependence of Cell Potential

1 Prepare 60 mL of a solution that is 0.10 *M* in ascorbic acid ($C_6H_8O_6$) and 0.10 *M* in sodium hydrogen phosphate ($Na_2HPO_4 \cdot 7\ H_2O$). You can weigh both solids into the 100 mL beaker and add 60 mL of deionized water to it afterwards. Gentle swirling should dissolve the solids quickly.

2 Using a hand-held pH meter, adjust the pH of the solution to pH 6.8 - 7.2 by adding 3 *M* HCl or 3 *M* NaOH dropwise. It should not take more than 20 drops of either.

3 Assemble the electrochemical cell with the Cu^{2+}/Cu couple as one half-cell and the buffered ascorbic acid solution with a graphite electrode as the other.

4 Measure the voltage. Make sure it is positive; if not, exchange the leads to the copper and graphite electrodes. Record the voltage and note which lead is connected to copper and which is connected to graphite in Table C.

5 Use a hand-held pH meter, and adjust the pH of the solution to pH 4.8 - 5.2. Use 3 *M* HCl added dropwise. 3 *M* NaOH is available if too much acid is added.

6 Reassemble the cell, with the leads in the same positions as they were in Step 4.

7 Measure and record the voltage in Table C.

8 When you are finished, rinse the salt bridge and return it to the KNO_3 containers and close the lids. Replace the lids to any of the other solutions that are still open. Dispose of the waste rinsings and buffered ascorbic acid solution down the drain with plenty of water. Rinse all of your glassware with water, dry it and return it to the set-up area where you found it.

9 Please close the MicroLab program and turn off your pH meter.

10 Before leaving, enter your results in the in-lab assignment. If all results are scored as correct, log out. If not all results are correct, try to find the error or consult with your lab instructor. When all results are correct, note them and log out of WebAssign. The in-lab assignment must be completed by the end of the lab period. If additional time is required, please consult with your lab instructor.

Standard Reduction Potentials at 298 K vs SHE

Half Reaction			Potential
$Mg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mg(s)$	–2.36 V
$2H_2O + 2e^-$	$\rightleftharpoons$	$H_2(g) + 2OH^-(aq)$	–0.83 V
$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$	–0.76 V
$Pb^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Pb(s)$	–0.13 V
$2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2(g)$	0.00 V
$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34 V
$O_2(g) + 2H_2O + 4e^-$	$\rightleftharpoons$	$4OH^-(aq)$	+0.40 V
$I_2(s) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$	+0.54 V
$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$	+0.80 V
$O_2(g) + 4H^+(aq) + 4e^-$	$\rightleftharpoons$	$2H_2O$	+1.23 V
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightleftharpoons$	$Mn^{2+}(aq) + 4H_2O$	+1.51 V