Experiment 21

Voltaic Cells

INTRODUCTION:
A voltaic cell is a specially prepared system in which an oxidation-reduction reaction occurs spontaneously. The oxidation and reduction half-reactions are separated so that the current must run through an external wire. This spontaneous reaction produces an easily measured electrical potential. Common household batteries are actually voltaic cells.

We can predict the potential for any voltaic cell by using standard reduction potentials that are tabulated in the Appendix of your textbook. The potential of a cell can be calculated by combining the potentials of its half-reactions: $E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}}$. But, if you look at the table, you will find that all the reactions are listed as reductions. Which of the two half-reactions in our cell is actually the oxidation? Because spontaneous overall reactions have positive values of $E$, we know that the half-reaction with the smaller (more negative) half-potential will actually be an oxidation.

Tabulated reduction potentials are measured at standard conditions: 25°C, 1 atm, and 1 M concentrations for all solutions. That is nice, but we often aren’t working at standard conditions. In particular, we often have solution concentrations that aren’t 1 M. The potential for a cell operated at non-standard conditions can be calculated using the Nernst equation:

$$E = E^\circ - \frac{0.05916}{n} \log_{10} Q$$

where $E$ is the potential at non-standard conditions, $E^\circ$ is the potential at standard conditions, $n$ is the number of moles of electrons being transferred, and $Q$ is the reaction quotient. Recall that $Q$ has the same form as $K_{eq}$ but is for non-standard conditions.

In this experiment, you will prepare a variety of semi-microscale voltaic cells in a 24-well test plate. A voltaic cell is constructed by using two metal electrodes and solution of their respective salts (e.g., Cu in Cu$^{2+}$ or Zn in Zn$^{2+}$) with known molar concentrations. The set-up is shown on the next page. Note the short length of string draping between the two cells in the figure. It has been soaked in a solution of KNO$_3$ and serves as the salt bridge in our cell, completing the circuit. In lab, how can we tell which half-reaction is the oxidation? When your voltaic cell is set up and has positive value for the cell potential, the black connector wire is attached to the anode, the half-cell in which oxidation is occurring.

In Part I of this experiment, you will use a voltmeter to measure the potential of a voltaic cell with copper and zinc electrodes. You will then test two voltaic cells that have unknown metal electrodes paired with zinc. Through careful measurements of the cell potentials, you will identify the unknown metals (Part II). In Part III, you will measure the potential of a special type of voltaic cell called a concentration cell. Here the two electrodes are made of the same metal. Only the concentration of the electrolyte varies between the two sides. In the first concentration cell, you will observe how a voltaic cell can maintain a spontaneous redox reaction with identical copper metal electrodes, but different electrolyte concentrations. You will then measure the potential of two other cells and use the Nernst equation to calculate ion concentrations, which will in turn allow you to calculate values of equilibrium constants.
PRE-LAB ASSIGNMENT:
Copy the table below into your lab notebook. Use the table of standard reduction potentials in your textbook to complete the table. For each metal, look up the half-reaction for
\[ M^{2+} (aq) + 2e^- \rightarrow M(s) \]

Silver is an exception; there you want the Ag\(^{+}\) ion. Decide which half-reaction in each pair must be the oxidation in order to give a positive value of \( E^\circ_{\text{cell}} \) when the half potentials are added together. An example is provided.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Half-reactions</th>
<th>( E^\circ )</th>
<th>Oxidation</th>
<th>( E^\circ_{\text{cell}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>Zn(^{2+})(aq) + 2e(^-) \rightarrow Zn(s)</td>
<td>-0.76 V</td>
<td>Zn</td>
<td>+1.10 V</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu(^{2+})(aq) + 2e(^-) \rightarrow Cu(s)</td>
<td>+0.34 V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Pb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Ag</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Mg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Ni</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PROCEDURE:
This procedure will be done in pairs. Record the names of both partners in your lab notebook.

Part I: Determine the E for a Cu-Zn Voltaic Cell
1. Use a 24-well test plate as your voltaic cell. Use Beral pipets to transfer small amounts of 0.10 M Cu(NO\(_3\))\(_2\) and 0.10 M Zn(NO\(_3\))\(_2\) solution to two neighboring wells in the test plate.
2. Obtain one Cu and one Zn metal strip to act as electrodes. Polish each strip with steel wool. Place the Cu strip in the well of the Cu(NO\(_3\))\(_2\) solution and place the Zn strip in the well of the Zn(NO\(_3\))\(_2\) solution. These are the half cells of your Cu-Zn voltaic cell.
3. Make a salt bridge by soaking a short length of string in a beaker that contains a small amount of 1 M KNO\(_3\) solution. Connect the Cu and Zn half cells with the string as shown in Figure a.
4. Connect the leads from the voltmeter to the Cu and Zn electrodes to get a positive potential reading. (If you see a negative value, reverse the leads.) Record the potential immediately after making the connection. Record with metal was attached to the black connector wire.
5. Remove both electrodes from the solutions. Clean and polish each electrode. Measure the potential again.
6. Repeat for a third time, polishing each electrode and re-measuring the potential.
7. Record the metal attached to the black wire, the potentials from the three trials, and the mean value in a well-labeled data table in your lab notebook.
Part II: Determine the E for Two Voltaic Cells Using Zn and Unknown Metals X and Y
8. Obtain a small amount of the unknown electrolyte solution labeled “0.10 M X” and the corresponding metal strip, X. Clean the metal strip with steel wool.
9. Use a Beral pipet to transfer a small amount of 0.10 M X Solution to a well adjacent to the 0.10 M Zn(NO$_3$)$_2$ solution in the test plate.
10. Make a new salt bridge by soaking a short length of string in the beaker of 1 M KNO$_3$ solution. Connect the X and Zn half cells with the string.
11. Measure the potential of the X-Zn voltaic cell three times, following the same general procedure used before, cleaning the metal strips with steel wool each time. Again, record your data and the mean value in a well-labeled table. Be sure to note which metal the black electrode was attached to.
12. Repeat steps 8-11 using the unknown metal strip Y and its corresponding electrolyte solution, 0.10 M Y.

Part III: Prepare and Test Three Concentration Cells
13. Set up and test a copper concentration cell.
   a. Prepare 20 mL of 0.050 M CuSO$_4$ solution by mixing 1 mL of 1.0 M CuSO$_4$ solution with 19 mL of distilled water. (Note that this is not the same concentration solution you used in the Part I.)
   b. Set up a concentration cell in two wells of the 24-well test plate by filling one well about two-thirds full with 0.050 M CuSO$_4$ solution and an adjacent well two-thirds full with 1.0 M CuSO$_4$. (Save the rest of your 0.050 M CuSO$_4$ for step 14.) Use Cu metal electrodes in each well. Use a fresh KNO$_3$-soaked string as the salt bridge, as in Parts I and II.
   c. Test and record the potential of the concentration cell three times in the same manner that you tested the voltaic cells in the Parts I and II. Be sure you clean the metals each time.
14. Determine the formation constant of Cu(NH$_3$)$_4^{2+}$.
   a. Mix 5 mL of 0.050 M CuSO$_4$ solution with 5 mL of 3.0 M NH$_3$ solution in a small beaker. Note that by mixing, we dilute the reactants. You now have 10 mL of 0.025 M CuSO$_4$ and 1.5 M NH$_3$ as the initial mixture before reaction.
   b. Fill a well adjacent to the 0.050 M CuSO$_4$ well two-thirds full with the solution prepared in the step 14a.
   c. Complete the cell with clean copper electrodes and a KNO$_3$-soaked string as the salt bridge.
   d. Test and record the potential of the cell as in step 13c.
15. Determine the solubility product constant, $K_{sp}$, of PbI$_2$.
   a. Prepare about 10 mL of 0.050 M Pb(NO$_3$)$_2$ solution by diluting 5 mL of 0.10 M Pb(NO$_3$)$_2$ solution with distilled water.
   b. Mix 9 mL of 0.050 M KI solution with 3 mL of 0.050 M Pb(NO$_3$)$_2$ solution in a small beaker. Note that by mixing, we dilute the reactants. You now have 12 mL of 0.0375 M KI and 0.0125 M Pb(NO$_3$)$_2$ as the initial mixture before reaction.
   c. Set up the half cells in neighboring wells of the 24-well test plate. In one cell use the solution prepared in the previous step. In the other well, use 0.050 M Pb(NO$_3$)$_2$ as your electrolyte solution. Use Pb electrodes in each half cell. Use a KNO$_3$-soaked string as the salt bridge.
   d. Test and record the potential of the cell in the same manner that you tested the voltaic cells in Part I. Be sure to take three measurements.
16. Discard the electrodes and the electrolyte solutions as directed. Rinse and clean the 24-well plate and return it to the reagent bench.
RESULTS AND DISCUSSION:
You will need several data tables for your Results Section. For Part I, prepare a well-organized and labeled data table. Include all the data you collected in the lab and the predicted value of $E^{\circ}_{\text{cell}}$ for the Cu-Zn cell that you calculated in the pre-lab assignment from the tabulated standard reduction potentials. For Part II, prepare a well-labeled data table that includes all of your data and also gives the identity of metals X and Y. To identify these metals, compare your experimentally measured values of $E^{\circ}_{\text{cell}}$ to the predicted values that you calculated in the pre-lab assignment.

For each of the three systems in Part III, you will need to do some calculations using the Nernst equation. For the copper concentration cell, the net cell reaction is

$$\text{Cu}^{2+}\text{(more concentrated)} + \text{Cu(s)} \rightarrow \text{Cu}^{2+}\text{(more dilute)} + \text{Cu(s)}$$

Use your experimentally measured mean value of $E$, the Nernst equation, and the given concentration of $\text{Cu}^{2+}$, concentrated] to calculate an experimental value for $\text{Cu}^{2+}$, dilute]. Not that $E^{\circ} = 0$ since we have the same half-reaction on each side. Figure out the value of $n$. Substitute your value of $\text{Cu}^{2+}$, concentrated] into the expression for $Q$. Now solve for $\text{Cu}^{2+}$, dilute]. Show sample calculations, and summarize your values in a well-labeled table that includes values for $E$, $\text{Cu}^{2+}$, concentrated], $n$, experimental $\text{Cu}^{2+}$ dilute], and the intended $\text{Cu}^{2+}$, dilute]. The intended $\text{Cu}^{2+}$, dilute] is the concentration of the more dilute half cell from the procedure.

The formation constant of Cu(NH$_3$)$_4$$^{2+}$ calculation starts with the same step as the calculation you just completed for the copper concentration cell. As before, use your experimental mean value of $E$ and $\text{Cu}^{2+}$, concentrated] in the Nernst equation to calculate $\text{Cu}^{2+}$, dilute]. This is the $\text{Cu}^{2+}$ at equilibrium.

We will now use this $\text{Cu}^{2+}$ at equilibrium to calculate the formation constant of Cu(NH$_3$)$_4$$^{2+}$, i.e., the value of $K_{eq}$ for

$$\text{Cu}^{2+}\text{(aq)} + 4 \text{NH}_3\text{(aq)} \rightarrow \text{Cu(NH}_3)_4$$^{2+}\text{(aq)}$$

In order to calculated the value of $K_{eq}$, we need to know equilibrium values of $\text{NH}_3$ and $\text{Cu(NH}_3)_4$$^{2+}$] in addition to the value of $\text{Cu}^{2+}$ you just calculated. The easiest way to work through this calculation is with an ICE table (the initial/change/equilibrium table we typically use for equilibrium problems). Set up an ICE table. In the initial line record the concentrations of CuSO$_4$ and NH$_3$ that were initially present before reaction as noted in the procedure. Complete all three rows of the ICE table as usual, using $–x$ for the amount of $\text{Cu}^{2+}$ in the change line. Be sure to pay careful attention to the mole ratios in the change line.

We know that value of $\text{Cu}^{2+}$ at equilibrium because you calculated it with the Nernst equation. Set this equal to the expression for $\text{Cu}^{2+}$ at equilibrium from your ICE table and solve for $x$. Now that you know the value of $x$, use it to find the equilibrium concentrations of $\text{NH}_3$ and $\text{Cu(NH}_3)_4$$^{2+}$]. Write the expression for $K_{eq}$, plug in the values of your equilibrium concentrations, and solve for the value of $K_{eq}$. Show sample calculations (your ICE table) and summarize your values in a well-labeled table including values for $E$, $\text{Cu}^{2+}$] at equilibrium, $x$, $\text{Cu(NH}_3)_4$$^{2+}$] at equilibrium, $\text{NH}_3$] at equilibrium, and $K_{eq}$.

The solubility product of PbI$_2$ calculation is very similar to the one you just completed for the formation constant. Substitute your experimental mean value of $E$ and $\text{Pb}^{2+}$, concentrated] from the procedure into the Nernst equation and calculate $\text{Pb}^{2+}$, dilute]. We will now use this $\text{Pb}^{2+}$ at equilibrium to calculate the solubility product constant of PbI$_2$, i.e., the value of $K_{sp}$ for

$$\text{PbI}_2(s) \leftrightarrow \text{Pb}^{2+}(aq) + 2\text{I}^-(aq)$$
Again, set up an ICE table. Follow the same general procedure for calculations that you used above. Show sample calculations (your ICE table), and summarize you values in a well-labeled data table including values for $E$, $[\text{Pb}^{2+}]$ at equilibrium, $x$, $[I^-]$ at equilibrium, and $K_{sp}$.

**QUESTIONS:**

1. Explain how you identified unknowns X and Y. Discuss any uncertainty in your identifications.

2. Look up concentration cells in your textbook. Explain how they are similar to and different from more typical voltaic cells.

3. What is the job of the salt bridge in a voltaic cell? Look this up in your textbook. Explain as completely as you can why a salt bridge is needed.