Galvanic Cells

INTRODUCTION

In a redox reaction, electrons are transferred from a reducing agent to an oxidizing agent. An electrochemical cell is a mechanical device in which the transfer of electrons occurs through a wire. The electron flow through the wire is an electric current. Electrochemistry is the study of the relationship between chemical change and electrical work. Electrochemical processes always involve the movement of electrons from one species to another in an oxidation-reduction (redox) reaction. This redox reaction may either produce or use electrical energy.

The overall redox reaction is composed of two half-reactions, the oxidation and reduction half-reactions shown below:

**oxidation** (loss of electrons): \[ X \rightarrow X^{n+} + \text{ne}^- \]

**reduction** (gain of electrons): \[ Y^{m+} + \text{me}^- \rightarrow Y \]

In an electrochemical process, the oxidation half-reaction always takes place at the anode. The site of the reduction reaction is defined as the cathode.

GALVANIC CELLS

A Galvanic cell (or voltaic cell), utilizes a spontaneous oxidation-reduction reaction to produce electrical energy. To help us understand the process, we can think of a Galvanic cell as being composed of two half-cells, one of which is the site of oxidation (the anode) and the other the site of reduction (the cathode).

The overall voltage of the cell depends upon the nature of the half-cell combinations. Half-cells normally consist of a piece of metal placed in a solution containing a cation of the metal (such as copper metal in a solution containing copper (II) ions from dissolved copper (II) nitrate). The spontaneous reaction in the Galvanic cell consists of a reduction half-cell reaction that takes place at the cathode and an oxidation half-cell reaction that takes place at the anode. The overall voltage of the cell can be calculated using the formula:

\[ \mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{red, cathode}} + \mathcal{E}_{\text{ox, anode}} \]

where \( \mathcal{E}_{\text{red, cathode}} \) is the reduction potential for the cathode half-cell reaction, and \( \mathcal{E}_{\text{ox, anode}} \) is the oxidation potential for the anode half-cell reaction. Because half-cell potentials are found in tables showing only reduction potentials, the reduction half-cell reaction at the cathode will be the half-cell reaction with the greater reduction potential. The oxidation half-cell reaction at the anode will be the reverse of the half-cell reaction with the lesser reduction potential. With the half-cell reaction with the lesser reduction potential being reversed to become an oxidation, the oxidation potential for the anode half-cell reaction will be the negative of the reduction potential.

For Part A of the experiment, a number of Galvanic cells will be prepared using metal electrodes, 1.0 M electrolyte solutions and a porous salt bridge. Using a voltmeter, we will touch the positive (+) electrode to one metal and the negative (-) electrode to another. If a positive voltage is recorded, we have connected the galvanic cell correctly; that is, there is a flow of electrons from the anode to the cathode. A negative voltage means that the leads must be reversed to generate a Galvanic cell.
By comparing the voltage values obtained for several pairs of half-cells where one metal is chosen to always be the anode (in this experiment, we will choose copper), you can establish a table of metals which reflects the relative tendency of the metal to undergo oxidation or reduction. You can then create other Galvanic cells by using your table to predict which will be the anode and the cathode. The cell potential of these other Galvanic cells will be measured in Part B and their values will be compared to potential calculated from the data in Part A and the potential calculated from textbook values.

Finally, we will investigate the effect of concentration on the cell potential by using a concentration other than 1 M for one of the electrolytes.

The effect of electrolyte concentration on cell potential can be described by the Nernst equation. The Nernst equation for a cell at 25°C is represented by the following equation:

\[ \mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cell}}^\circ - \frac{RT \ln Q}{NF} \]

where \( \mathcal{E}_{\text{cell}}^\circ \) is the standard cell potential, R is the Universal Gas Constant, n is the number of electrons involved in the redox reaction, \( F \) is Faraday’s Constant (the charge, measured in Coulombs, equivalent to one mole of electrons), and the \( Q \) is the reaction quotient.

To explore the effect of concentration on cell potential, in Part C we will use the Cu|Cu²⁺||Ag⁺|Ag cell.

**PROCEDURE**

1. Students will work individually for this experiment. Except for the laboratory handout, remove all books, purses, and such items from the laboratory bench top, and placed them in the storage area by the front door. For laboratory experiments you should be wearing closed-toe shoes. Tie back long hair, and do not wear long, dangling jewelry or clothes with loose and baggy sleeves. Open your lab locker. Put on your safety goggles, your lab coat, and gloves.

**PART A – TESTING VOLTAIC CELLS**

2. Obtain a piece of filter paper and a Petri dish. Place the Petri dish on top of the filter paper, and trace out a circle. Using a pair of scissors cut the filter paper slightly smaller than the drawn circle in order for it to fit inside the Petri dish during the experiment.

3. On the filter paper draw six small circles in pencil, equally spaced, close to the edge of the filter paper, as shown in Figure 1 on the next page. Label the circles Cu, Zn, Pb, Ag, Mg, and Fe. Draw a line from the center of each circle to the center of the filter paper.

4. Using a pair of scissors, cut out wedges of filter paper between the circles to create the wings as shown in Figure 2 on the next page. Place the filter paper in a Petri dish.

5. Obtain small pieces of the six metals mentioned above. Carefully clean both sides of each piece of metal with emery cloth (sand paper) to remove any metal oxide coating. For each metal there is a corresponding 1.0 M aqueous solution of its cation. As shown in Figure 3 on the next page, place 1 drop of each metal solution on its corresponding circle (Fe²⁺ on Fe, Ag⁺ on Ag, etc.), then place the corresponding piece of metal on the wet spot keeping the top side of the metal dry. *Avoid skin contact with the Ag⁺ (aq) solution.*
6. Using a capillary tube, add several small drops of 1.0 M NaNO₃ on a line from each piece of metal to the center of the filter paper, as shown above in Figure 3. The drops should form a continuous wet path that connects the pieces of metal. You may need to periodically dampen the filter paper with your solutions during the course of the experiment.

7. Obtain a multimeter, and red and black cables with alligator clips from the cart. Plug the black cable into the COM input jack and the red cable into the positive input jack (the right-most jack). Turn the function switch (the dial) on the multimeter to the 2 V setting (the one with the solid line and dotted line above it), making it a voltmeter. Pull the alligator clips off of the ends of the red and black cables, exposing the sharp metal electrodes.

8. Use copper as the reference metal initially. This means that copper will be the (-) pole. Measure the potential of the five cells all relative to copper (Zn to Cu, Pb to Cu, Ag to Cu, etc.) by bringing the electrode attached to the black lead (anode) in contact with Cu and the electrode attached to the red lead (cathode) in contact with the other metal. Wait about 5 seconds to take a voltage reading.

**NOTE:** If the recorded voltage from the voltmeter is positive, the metal being tested has a greater tendency to be reduced than copper. However, if the recorded voltage from the voltmeter is negative, the metal being tested has a lesser tendency to be reduced than copper.

Record the value and sign appearing on the voltmeter in your Data Table. **Record all voltage readings to the hundredths place.**

9. By assigning copper an arbitrary voltage of 0.00 V, we can determine the relative reduction potentials of the other six metals by using equation

\[ \mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{red, cathode}} + \mathcal{E}_{\text{ox, anode}} \]

Since copper was the anode in each galvanic cell, we can substitute 0.00 V for \( \mathcal{E}_{\text{ox, anode}} \) and therefore calculate the reduction potential of the other six metals (\( \mathcal{E}_{\text{red, cathode}} \)) by using the measured cell potential recorded from the voltmeter. Because the most active metals are the ones that undergo oxidation most readily, the metals with the most negative reduction potentials are the most active. Using your calculated reduction potentials, you should be able to rank the six metals from most active to least active, which means from lowest reduction potential to highest reduction potential.
PART B – CREATING AN ACTIVITY SERIES

10. Using your same set-up from Part A, measure the cell potentials for the following five combinations:
   - lead and zinc
   - silver and iron
   - zinc and magnesium
   - iron and magnesium
   - silver and lead

   Since we are creating voltaic cells, the measured cell potentials should be positive. If the potential is not positive, reverse the leads on the voltmeter. Record the measured potential, which metal was touching the anode (the negative lead), and which metal was touching the cathode (the positive lead).

11. Compare your measured values to the predicted values using your potentials from Part A, and then compare your measured values to the predicted values using the potentials from the Appendix in the text.

12. When you have finished, use forceps to remove each of the pieces of metal from the filter paper. Rinse each piece of metal with deionized water, dry it, and return it to the plastic bag. Remove the filter paper from the Petri dish using the forceps, and throw it in the trash. Finally, rinse the Petri dish with deionized water and return it to the kit at your desk.

PART C – EFFECT OF CONCENTRATION ON CELL POTENTIAL

13. Using a procedure similar to the one described in the proceeding steps, prepare a piece of filter paper with only 2 wings, place it on a watch glass and construct the following cell.

   \[
   \text{Cu(s)} | \text{Cu}^{2+} (1.0 \text{ M}) \parallel \text{Ag}^+ (0.010\text{M}) | \text{Ag (s)}
   \]

14. Measure and record the potential. Compare your measured value to the predicted value using the potentials from the Appendix in the textbook and the Nernst equation.

15. When you have finished, use forceps to remove the pieces of metal from the filter paper. Rinse each piece of metal with deionized water, dry it, and place them in the plastic bag in the fume hood. Remove the filter paper from the Petri dish using the forceps, and throw it in the trash. Rinse the Petri dish with deionized water and return it to the kit at your desk. Finally, turn off the multimeter, replace the alligator clips back onto the sharp electrodes of the red and black cables, and return the multimeter and cables to the cart.

16. Clean and wipe dry your laboratory work area and all apparatus. When you have completed your lab report have the instructor inspect your working area. Once your working area has been checked your lab report can then be turned in to the instructor.
## DATA TABLE

### PART A

<table>
<thead>
<tr>
<th>Electrochemical Cell</th>
<th>Measured Cell Potential</th>
<th>$\varepsilon_{\text{metal red}}$ Relative to Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn, Zn$^{2+}$ and Cu, Cu$^{2+}$</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>Pb, Pb$^{2+}$ and Cu, Cu$^{2+}$</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>Ag, Ag$^+$ and Cu, Cu$^{2+}$</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>Mg, Mg$^{2+}$ and Cu, Cu$^{2+}$</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>Fe, Fe$^{2+}$ and Cu, Cu$^{2+}$</td>
<td>.</td>
<td>.</td>
</tr>
</tbody>
</table>

### PART B

<table>
<thead>
<tr>
<th>Electrochemical Cell</th>
<th>Measured $\varepsilon_{\text{cell}}$</th>
<th>Anode Metal</th>
<th>Cathode Metal</th>
<th>Calculated $\varepsilon_{\text{cell}}$ from Part A Data</th>
<th>Calculated $\varepsilon_{\text{cell}}$ from Book Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2 Pb, Pb$^{2+}$ &amp; Zn, Zn$^{2+}$</td>
<td>.</td>
<td>.</td>
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<td>.</td>
<td>V</td>
</tr>
<tr>
<td>3-4 Ag, Ag$^+$ &amp; Fe, Fe$^{2+}$</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>V</td>
</tr>
<tr>
<td>5-6 Zn, Zn$^{2+}$ &amp; Mg, Mg$^{2+}$</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>V</td>
</tr>
<tr>
<td>7-8 Fe, Fe$^{2+}$ &amp; Mg, Mg$^{2+}$</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>V</td>
</tr>
<tr>
<td>9-10 Ag, Ag$^+$ &amp; Pb, Pb$^{2+}$</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>V</td>
</tr>
</tbody>
</table>

### PART C

<table>
<thead>
<tr>
<th>Electrochemical Cell</th>
<th>Measured $\varepsilon_{\text{cell}}$</th>
<th>Calculated $\varepsilon_{\text{cell}}$ from Nernst Equation and Book Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 Ag, Ag$^+$ &amp; Cu, Cu$^{2+}$</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>CALCULATIONS</td>
<td></td>
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<tr>
<td>1.</td>
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<td>7.</td>
<td>8.</td>
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<td>9.</td>
<td>10.</td>
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</tbody>
</table>
**TRUE OR FALSE**

1. ____ In a Galvanic cell, oxidation occurs at the anode.

2. ____ In a Galvanic cell, the cell potential, \( \mathcal{E} \), equals \( \mathcal{E}_{\text{red, cathode}} + \mathcal{E}_{\text{red, anode}} \)

3. ____ In a Galvanic cell, electrons flow through a wire from anode to cathode.

4. ____ The greater the reduction potential of a metal, the more likely it is for its ion to be reduced.

5. ____ The greater the reduction potential of a metal, the more active it is.

6. ____ When the \( Q \) value for a reaction is > 1, its \( \mathcal{E}_{\text{cell}} > \mathcal{E}_{\text{cell}}^\circ \)

**QUESTIONS**

1. From the data in Part A, rank the six metals from the most active (most likely to be oxidized and \( \therefore \) least likely to be reduced) to least active (least likely to be oxidized and \( \therefore \) most likely to be reduced).

   Most active:  
   _____________________________    (lowest reduction potential)
   _____________________________
   _____________________________
   _____________________________
   _____________________________
   _____________________________

   Least active:  
   _____________________________    (highest reduction potential)
2. From Part B, write the anode half-reaction, the cathode half-reaction, and the overall reaction for each electrochemical cell.

Pb and Zn:
Anode: ___________________________  Cathode: ___________________________
Overall: _____________________________________________________________

Ag and Fe:
Anode: ___________________________  Cathode: ___________________________
Overall: _____________________________________________________________

Zn and Mg:
Anode: ___________________________  Cathode: ___________________________
Overall: _____________________________________________________________

Fe and Mg
Anode: ___________________________  Cathode: ___________________________
Overall: _____________________________________________________________

Ag and Pb
Anode: ___________________________  Cathode: ___________________________
Overall: _____________________________________________________________
3. A galvanic cell is made up of a copper electrode in a 1.0 M copper (II) sulfate solution, a silver electrode in a 1.0 M silver nitrate solution, and a salt bridge connecting them at 25ºC.

(a) On the diagram below, label the two electrodes as (1) anode or cathode, and (2) copper or silver. Label the two solutions as copper (II) sulfate or silver nitrate, and then show the flow direction of electrons through the wire.

(b) Write the spontaneous reaction for the Galvanic cell.

(c) Calculate the potential for the Galvanic cell.

(d) 6.0 M ammonia is added to the copper (II) sulfate solution until the Cu²⁺ ion is essentially all converted to the tetraamminecopper(II) complex ion. At this point the potential of the cell goes up to 0.92 V. Find the residual concentration of Cu²⁺ ion in the cell.