Experiment 18: Galvanic Cells and Corrosion

Objectives
- To explore the corrosion of iron and cathodic protection
- To construct galvanic cells
- To learn how reduction potentials can be used to predict the relative reactivity of metals

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 → X^{n+} + ne^-
reduction (gain of electrons): Y^{n+} + me^- → 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.

In the first part of today's experiment, you will be studying the corrosion of iron nails and whether contact with other metals can deter or accelerate this naturally occurring redox system. In second part of the experiment, you will construct galvanic cells in order to generate a table of reduction potentials.

Part 1: Corrosion of Iron:
Corrosion is a naturally occurring redox process that oxidizes metals to their oxides. Today we will be focusing primarily on the corrosion of iron. Iron undergoes a two-step oxidation process as follows:

step 1: Fe (s) → Fe^{2+} + 2 e^-
step 2: Fe^{2+} → Fe^{3+} + e^-
The final oxidation product, iron (III), then combines with oxygen and water to form iron(III) oxide, or what we call "rust".

In today's experiment you will determine which metals enhance the corrosion of iron and which inhibit the corrosion. You will test this by placing iron nails in contact with different metals and testing if corrosion of iron occurs. Since the corrosion process typically takes longer than your scheduled lab time, you will use color indicators to determine whether the iron is or is not corroding and where the oxygen is being reduced.

You will identify the regions in which iron is being oxidized (the anode) by the appearance of a blue color, caused by the reaction described below:

3 Fe^{2+} (aq) + 2 Fe(CN)_6^{3-} (aq) → Fe_3[Fe(CN)_6]_2 (s)

In this reaction, the Fe^{2+} are colorless ions in solution formed by the oxidation of iron. The complex ion, Fe(CN)_6^{3-}, will be added to your solution in the form of K_3[Fe(CN)_6] solid. The final product produced in the above reaction, Fe_3[Fe(CN)_6]_2 (s), is blue in color and indicates that iron was oxidized from Fe (s) to Fe^{3+}.

You will be able to identify where oxygen is being reduced (the cathode) by the appearance of a pink color. Oxygen is first reduced to hydroxide ions by the reaction shown below:

O_2 (g) + 2 H_2O (l) + 4e^- → 4 OH^- (aq)

The OH^- ions then react with the colorless phenolphthalein indicator and turn the phenolphthalein pink.

To summarize, if any blue color appears, then you know iron was oxidized from Fe to Fe^{3+}. If any pink color appears, then you know oxygen was reduced. Unfortunately, these are the only two indicators we have in solution. Other oxidation reactions are possible; however, there is no indicator available to detect their presence. By making careful observations of all the nail systems today, you should be able to deduce what other reactions may have occurred even if there was an absence of one of the colors.

Part 2: 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 (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 (e.g. Cu
metal in a solution of Cu(NO$_3$)$_2$ or Cu(II)). The overall voltage of the cell can be calculated using the following formula:

$$E_{\text{cell}} = E_{\text{red, cathode}} - E_{\text{red, anode}}$$

where $E_{\text{red, cathode}}$ is the reduction potential for the cathode reaction, and $E_{\text{red, anode}}$ is the reduction potential for the anode reaction. Note that the equation requires a reduction potential for the anode half-cell even though oxidation takes place at the anode. The negative sign in the equation takes into account that oxidation takes place at the anode.

For part 2a 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 (+) pole to one metal and the negative (-) to another. If a positive voltage is recorded, we have created a Galvanic cell. 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 copper is chosen to always be the anode, 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 2b and their values will be compared to potential calculated from the data in part 2a 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 1M 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:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q$$

where $E_{\text{cell}}^\circ$ is a constant for a given reaction and is called the standard cell potential, $n$ is the number of electrons involved in the redox reaction, and $Q$ is the reaction quotient.

To explore the effect of concentration on cell potential, we will use the Cu|Cu$^{2+}$|Ag$^+$|Ag cell.

**Procedure:**

### Part 1: Corrosion

1. Heat 100 mL of deionized water to boiling in a 250-mL beaker using your hot plate. While the water is heating, prepare 5 sandpapered nails as follows (see figure below as well):

   - Pierce a small piece of zinc with a nail
   - Pierce a small piece of copper with a nail
   - Score a nail with a metal file in several places.
   - Keep one nail intact
   - Pierce a small piece of copper with a nail, wrap one piece of a piece of copper wire around the head of a nail, and wrap the other end around a piece of zinc.

2. Once the water has begun to boil, take the beaker off the hot plate and stir in 0.7 g of agar in four portions. **Don't add the agar all at once, it won't dissolve well.** After the agar dissolves, stir in 0.5 g of NaCl, 0.07 g of K$_3$[Fe(CN)$_6$] and 15 drops of phenolphthalein solution. Stir until all of the solids dissolve.

3. Cool the gel-indicator solution until it is just lukewarm or begins to thicken. Arrange your 5 nails in 5 large test tubes.

4. Pour the cooled agar mixture over the nails so as to cover them except the 2 plain nails; leave part of them out of the agar. Watch the tubes over a period of 20 minutes to an hour. Note the appearance of any colors around the nail assemblies. Record your observations in your notebook.

5. Once you have recorded your observations, scrape the agar and nails into their appropriate waste containers.

6. For each of the nail set-ups, you will need to determine in which set-up the iron is corroding and which systems there is a metal other than iron corroding. Determine the reactions at both the anode and cathode for each nail.
Part 2: Testing of Micro-Voltaic Cells; Creating an Activity Series

Part 2a
1. Obtain a piece of filter paper and draw six small circles, equally spaced, close to the edge of the filter paper. Label the circles Cu, Zn, Pb, Ag, Mg, and Fe and draw a line from the center of each circle to the center of the filter paper. Using a pair of scissors, cut out wedges of filter paper between the circles to create the wings shown below in the figure below:

Place the filter paper on the back side of a watch glass.

2. 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. 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⁺ solution.

3. Using a Pasteur pipet or 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. 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.

4. We will be using 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 (-) lead (black) in contact with Cu and the (+) lead (red) in contact with the other metal. Wait about 5 seconds to take a voltage reading and record the value and sign appearing on the voltmeter.

5. By assigning copper an arbitrary voltage of 0.00 V, we can determine the relative reduction potentials of the other six metals by using the relationship below where both the cathode half-cell potential (Eₐₙ₉ₐₜ₉ₑ₉₉) and anode half-cell potential (Eₐ₉ₙ₉ₐ₉ₑ₉₉) are reduction potentials. Since copper was always the (-) lead, we can substitute 0.00 V for Eₐ₉ₙ₉ₐ₉ₑ₉₉, and therefore calculate the reduction potential of the other six metals (Eₐ₉₉ₑ₉₉) by using the measured cell potential recorded from the voltmeter. Using these reduction potentials, rank the six metals from the highest to the lowest tendency to be the anode (site of oxidation). Note that if the recorded voltage from the voltmeter was negative, copper would have a greater tendency to be the cathode; however, since copper was always the (-) lead, copper is treated as the anode for the purposes of this calculation.

Part 2b
1. Using your same set-up from Part 2, measure the cell potentials for the following five combinations (or those designated by your instructor):
   - 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 and which lead (+ or -) was touching which metal.

2. Compare your measured values to the predicted values (using your potentials from Part 2a), and the theoretical values (using the potentials from the Appendix in the text).

3. 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 2c
1. Using a procedure similar to the one described in the preceding steps, prepare a piece of filter paper with only 2 wings, place it on a watch glass and construct the following cell:

   Cu(s) | Cu²⁺ (1.0 M) | | Ag⁺ (0.010M) | Ag (s)

2. Measure and record the potent
Experiment 18: Galvanic Cells and Corrosion
Pre-Lab Assignment

1. Sketch a Pb, Pb\(^{2+}\)/Zn, Zn\(^{2+}\) galvanic cell using the figure below. Look up the standard reduction potentials to determine which electrode is the cathode and which is the anode. Be sure to clearly label the cathode, anode, the direction of electron flow and the direction of ion flow. Then calculate the E\(^{\circ}_{\text{cell}}\) potential for this cell using standard reduction potentials.

![Galvanic Cell Diagram](image)

\[ E^{\circ}_{\text{cell}} \]

2. A student measures the potential of a cell made up with 1.0 M CuSO\(_4\) in one solution and 1.0 M AgNO\(_3\) in the other. There is a Cu electrode in the CuSO\(_4\) and a Ag electrode in the AgNO\(_3\). A salt bridge connects the 2 half cells. The student finds that the potential, or voltage of the cell, E\(^{\circ}_{\text{cell}}\) is 0.45 V and that the Cu electrode is negative.

   a. At which electrode is the oxidation occurring?

   b. Write the equation for the oxidation reaction.

   c. Write the equation for the reduction reaction.

   d. Write the overall equation for the reaction.

   e. The student adds 6.0 M NH\(_3\) to the CuSO\(_4\) solution until the Cu\(^{2+}\) ion is essentially all converted to Cu\((NH_3)_4\)\(^{2+}\) ion. The voltage of the cell, E\(_{\text{cell}}\), goes up to 0.92 V and the Cu electrode is still negative. Find the residual concentration of Cu\(^{2+}\) ion in the cell. (Use the Nernst Equation)
Exp. 18 Galvanic Cells and Corrosion: Data and Results

### Part 1: Corrosion

Record your results based on what you observed in this part in the table below. Answer the questions as asked. **Also write out** the anodic and cathodic reactions for what’s occurring in each case. **Draw your observations, or paste in photos, of color changes below the table, for each nail and metal combo.**

<table>
<thead>
<tr>
<th>Nail description</th>
<th>Did you see blue?</th>
<th>What metal is the Anode?</th>
<th>What metal is the Cathode?</th>
<th>Half-Cell Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain Nail</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scored Nail</td>
<td></td>
<td></td>
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<tr>
<td>Nail piercing Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nail piercing Cu</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Nail + Cu + Zn</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Name: ___________________________ Lab Day/Time: ____________
Partner: ___________________________
In which of the reactions in this part are the iron nails undergoing corrosion? List the cases in which you observe corrosion of the nail and tell me HOW you know the nail itself is corroding.

For those cases above in which the nail is not undergoing corrosion, what metals are corroding instead of iron? List these metals below, and tell me HOW you know this other metal is corroding.

How can you PREDICT which metal will corrode in the presence of another (when conditions are optimal for corrosion)?

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**Part 2a: Testing of Galvanic Cells**

Record in the table below, is the experimental voltage (both value and sign) for the following cells when the black (-) lead is in contact with Cu.

<table>
<thead>
<tr>
<th>Electrochemical Cell</th>
<th>Zn, Zn^{2+}/Cu, Cu^{2+}</th>
<th>Pb, Pb^{2+}/Cu, Cu^{2+}</th>
<th>Ag, Ag^{+}/Cu, Cu^{2+}</th>
<th>Mg, Mg^{2+}/Cu, Cu^{2+}</th>
<th>Fe, Fe^{2+}/Cu, Cu^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured Voltage</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
If you assign Cu an arbitrary electrode potential value of 0.00 V, the numbers above are the reduction potentials for the other metals relative to copper. In the table below, rank each of the metals from highest to lowest tendency to be the anode. Include Cu in your list.

| Tendency to be Oxidized (Metal) | E_{metal \, \text{red}} (V) \text{ Relative to Cu} | Reduction Half Reaction for each Metal
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td></td>
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</tr>
</tbody>
</table>

From your reduction potentials in the table above, list which metal or metals could protect iron from rusting. Explain your choices.

Part 2b: Predicting Cell Potentials

- Decide which metal should be the anode and which the cathode in order to create a galvanic cell (use the reduction potentials from part 2a).
- Then measure the cell potential with the voltmeter. Write the measured \( E_{\text{cell}} \) in the table.
- Calculate predicted \( E_{\text{cell}} \) values using the reduction potentials found in part 1a using the equation,
  \[
  E_{\text{cell}} = E_{\text{red, cathode}} - E_{\text{red, anode}}
  \]
- Calculate theoretical \( E^{\circ}_{\text{cell}} \) values using the reduction potentials given in the Appendix of your textbook and the equation,
  \[
  E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red, cathode}} - E^{\circ}_{\text{red, anode}}
  \]
<table>
<thead>
<tr>
<th>Cell</th>
<th>Anode metal</th>
<th>Cathode metal</th>
<th>Measured $E_{\text{cell}}$ (measure this)</th>
<th>$E_{\text{cell}}$ (from data in Part 2a)</th>
<th>$E^\circ_{\text{cell}}$ (from data in book)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, Pb$^{2+}$</td>
<td>Zn, Zn$^{2+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag, Ag$^+$</td>
<td>Fe, Fe$^{2+}$</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Zn, Zn$^{2+}$</td>
<td>Mg, Mg$^{2+}$</td>
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<td></td>
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</tr>
<tr>
<td>Fe, Fe$^{2+}$</td>
<td>Mg, Mg$^{2+}$</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ag, Ag$^+$</td>
<td>Pb, Pb$^{2+}$</td>
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</tbody>
</table>

For the Pb, Pb$^{2+}$/Zn$^{2+}$, Zn cell only, write the half reactions occurring at the anode and the cathode and write the overall reaction:

Anode: 

Cathode: 

Overall:

For the silver and iron cell, how did you decide which metal should be the anode and which the cathode?

Show your calculation of Predicted $E^\circ_{\text{cell}}$ using data from Part 2a for the silver and iron cell.

Show your calculation of Theoretical $E^\circ_{\text{cell}}$ silver and iron cell.
**Part 2c: Concentration Effects**

**Measured Potential, \( E_{\text{cell}} \), ____________

Calculate the **expected** cell potential using the Nernst Equation. Show your work.

**Follow-up Questions:**

A key part of lab is understanding what effect mistakes may have on results. For each mistake made, decide how the effect listed may have been affected by the mistake and **briefly** explain your answer. (Saying their results would be “off” or “altered” is not sufficient.)

<table>
<thead>
<tr>
<th>Student fails to add ( K_3\text{Fe(CN)}_6 ) to their agar solution in part 1.</th>
<th><strong>Effect on corrosion results:</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Student used 0.010 M solutions of both ( \text{Cu}^{2+} ) and ( \text{Ag}^+ ) in part 2c.</td>
<td><strong>Effect on the measured potential:</strong></td>
</tr>
</tbody>
</table>