Electrochemistry

INTRODUCTION:

The Electrochemical Cell

As we will learn in lecture, a reduction-oxidation (redox) reaction occurs due to a transfer of electrons from one substance to another. This transfer of electrons can generate an electrical current (flow of electrons), which can be measured and utilized to do work (e.g., power lights, your phone, your car, etc.). However, in order to measure this electrical current, we need to physically separate the two substances from each other and force the electron flow to occur through a wire. This is the basis for an **electrochemical cell**, a device that generates electricity through redox reactions. If the redox reactions are spontaneous, it is called a **galvanic cell** (or **voltaic cell**), and if nonspontaneous, it is referred to as an **electrolytic cell**. The cells we will be constructing and measuring in this lab are galvanic cells. A generic galvanic cell is shown in Figure 1 below.

![Galvanic Cell Schematic](image)

**Figure 1.** Galvanic Cell Schematic

The galvanic cell is comprised of two half-cells, a salt bridge, and a measuring device (the voltmeter). The **half-cells** are constructed by placing a metal in a solution containing its ions. For example, the copper half-cell for your first experiment is made by placing the copper...
wire in a solution of Cu(NO$_3$)$_2$ (a source of Cu$^{2+}$ ions) and the magnesium half-cell is made by placing the magnesium strip in a solution of Mg(NO$_3$)$_2$ (a source of Mg$^{2+}$ ions). The electrons generated or lost in the redox reactions enter or leave the respective half-cells through the conductive metal (herein referred to as the electrode), which simultaneously acts as a source of Cu(s) and Mg(s). The electrode where oxidation occurs is referred to as the anode and the electrode where reduction occurs is the cathode. In a galvanic cell, the anode is more negatively charged and is labeled as negative and the cathode is more positively charged and labeled as positive, with electrons flowing from the anode to the cathode as shown in Figure 1.

As electrons flow from the anode to the cathode, there is a buildup of charge in the solution, with excess negative charge in the cathode half-cell and positive charge in the anode half-cell. Left to continue building up, the electron flow would stop unless there is a pathway to complete the electrical circuit. This pathway is facilitated by the flow of counter ions in each half-cell connected by a salt bridge. The salt bridge is a concentrated source of ions without allowing the two half-cell solutions to mix. Typically, it is fabricated using a U-shaped glass tube filled with a salt-saturated gel, such as the one we will be using in this lab. The gel is comprised of 1.0M KNO$_3$ with a gelling agent added. The gelling agent is a material called Agar, which is a polymer that contains repeating units of agarose. This salt bridge allows for the flow of ions to neutralize the charge build-up in solution; anions in the bridge flowing to the positive build-up of charge at the anode and cations flowing to the cathode to neutralize the negative charge build-up at that electrode. It is important that ions chosen for the salt bridge are common with the ions in your half-cell solutions. What do you think the problem will be if we use a KCl salt bridge for our electrochemical cells?

In each half-cell, the metal reaches equilibrium with the ions in solution by the half-reactions shown:

- Cu(s) ⇌ Cu$^{2+}$(aq) + 2e$^-$
- Mg(s) ⇌ Mg$^{2+}$(aq) + 2e$^-$

The position of the equilibrium is different for differing metals and depends on the ease of ionization of each metal. The easier it is to ionize, the further to the right the equilibrium lies and the more electrons generated. If the two half-cells are connected by a wire, the electrons will flow (current) from the more negative half-cell to the more positive one. This results in oxidation at one metal and reduction at the other. The higher the current, the more electrons are flowing. The driving force in the electron flow is a difference in potential energy between the electrodes. This potential difference is measured as a voltage defined as:

$$1 \text{ volt} = 1 \text{ joule/coulomb} \quad (V = J/C)$$

This means that a charge of 1 coulomb experiences an energy difference of 1 joule between two electrodes. The larger the voltage, the larger the difference in potential energy, and the stronger the electron flow.
**Standard Potentials**

Each half-reaction has a standard potential referred to as the standard electrode potential, which are represented as reduction reactions. You will find a table below that lists the standard electrode potentials for several common reduction reactions. For example, for the 2-electron reduction of magnesium ion to magnesium metal, the following information can be found in the table:

\[
\text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg}(s) \quad E^\circ(V) = -2.37V
\]

And that for copper is:

\[
\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \quad E^\circ(V) = +0.34V
\]

Standard electrode potentials that are positive have a greater tendency to undergo reduction and those that are negative values have a lesser tendency to undergo reduction (i.e., more likely to undergo oxidation). Looking at our values above, we find that magnesium has a negative value for the reduction reaction, which tells us that it is more likely to undergo oxidation under standard conditions.

In a galvanic cell, the potential difference between the two electrodes is called the **cell potential** \(E_{\text{cell}}\). The \(E_{\text{cell}}\) depends on reactant and product concentrations and the temperature. If the concentrations are all 1M and the temperature is 25°C (standard conditions), then the cell potential is referred to as the **standard cell potential**, \(E^\circ_{\text{cell}}\). The overall standard cell potential is then the difference between two standard electrode potentials:

\[
E^\circ_{\text{cell}} = E^\circ_{\text{cat}} - E^\circ_{\text{an}}
\]

(\textit{where } E^\circ_{\text{cat}} \textit{ is the standard electrode potential for the cathode and } E^\circ_{\text{an}} \textit{ is the standard electrode potential for the anode.})

The cell potential is a measure of the tendency for the overall reaction to occur spontaneously. If the cell potential is low, there is a low tendency, if it is high, there is a high tendency, and if the number is negative, the forward reaction is not spontaneous.

Referring to our experiment where one of our half-cells is magnesium metal oxidized to magnesium ion in the presence of magnesium nitrate and the other half-cell is copper ion (in the form of copper nitrate) reduced to copper metal at the copper electrode. The half-reactions are:

- **Oxidation (anode):** \(\text{Mg}(s) \rightarrow \text{Mg}^{2+}(aq) + 2e^- \quad E^\circ(V) = -2.37V\)
- **Reduction (cathode):** \(\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \quad E^\circ(V) = +0.34V\)

The overall redox reaction then is:

\[
\text{Mg}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{Cu}(s) \quad E^\circ_{\text{cell}} = 0.34 - (-2.37) = +2.71V
\]
The standard cell potential is a positive value when magnesium is the anode and copper the cathode, so it is predicted that this combination of half-cells is spontaneous and will proceed in the forward direction. To predict which combination of half-cells gives a spontaneous reaction, consult the table of standard electrode potentials of two half-reactions of interest and calculate the standard cell potential. Note that even though we reverse the magnesium reaction to express it as an oxidation, the cell voltage stays the same.

Before coming to lab, determine which combinations of half-cells of Ag/AgNO$_3$, Cu/Cu(NO$_3$)$_2$, and Mg/Mg(NO$_3$)$_2$ will produce spontaneous redox reactions and their standard cell potentials. Indicate which is the oxidation reaction and which is the reduction reaction.

Knowing that a positive standard cell potential indicates that a reaction, as written, will proceed in the forward direction, we can relate $E^\circ_{\text{cell}}$ to the equilibrium constant, $K_{eq}$. Recall that a $K_{eq} > 1$ indicates the reaction will proceed in the forward direction and a $K_{eq} < 1$ indicates it will occur in the reverse direction. Utilizing this relationship, the following equation can be derived:

$$E^\circ_{\text{cell}} = \frac{0.0592 \, V}{n} \log K_{eq}$$  \hspace{1cm} (2)

(where $n =$ moles of electrons transferred in the redox reaction)

For each electrochemical cell you are to construct, calculate $K_{eq}$ from the previously determined standard cell potentials.

When describing electrochemical cells, it is convenient to use a short-hand notation called a cell diagram (also referred to as line notation). This diagram indicates the two half-reactions (minus the spectator ions), separated by the salt bridge represented with a double vertical line. When there are substances in differing phases, we separate those with a single vertical line. For example, for our first electrochemical cell in this lab (Figure 1), we write the cell diagram as:

$$\text{Mg}(s) \mid 1\text{M Mg}^{2+}(aq) \parallel 1\text{M Cu}^{2+}(aq) \mid \text{Cu}(s)$$

Notice that the oxidation half-cell is represented on the left and the reduction on the right with the ion concentrations indicated.

Before coming to lab, write the cell diagram for the electrochemical cells you determined above.

Influence of Concentration on Cell Potential

So far, the voltages we have been looking at have been for cells under standard conditions (i.e., 25°C and 1M). What happens to the cell potential if the concentrations are not 1M? If we revisit our overall reaction for the first cell: Mg(s) + Cu$^{2+}$(aq) $\rightarrow$ Mg$^{2+}$(aq) + Cu(s)
A decrease in Cu\(^{2+}\) (or Mg\(^{2+}\)) concentration is decreasing a reactant (or product) concentration from standard conditions. We can use Le Chatelier’s principle to predict which direction the reaction will shift to return to equilibrium and the influence on the cell voltage. The Nernst equations provides a relationship between \(E_{\text{cell}}\) under nonstandard conditions and \(E^\circ_{\text{cell}}\).

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q
\]  
(Nernst equation)  
(3)

Where \(E_{\text{cell}}\) is the cell potential (in Volts), \(E^\circ_{\text{cell}}\) is the standard cell potential, \(n\) is the number of electrons transferred per mole of the reaction, and \(Q\) is the reaction quotient. You will notice that under standard conditions \((Q = 1)\), \(E_{\text{cell}} = E^\circ_{\text{cell}}\). When a redox reaction occurs under conditions where \(Q < 1\), \(E_{\text{cell}} > E^\circ_{\text{cell}}\). When \(Q > 1\), \(E_{\text{cell}} < E^\circ_{\text{cell}}\). As the redox reaction reaches equilibrium, \(Q = K\) and the cell potential is equal to zero. Substituting \(K\) in for \(Q\) in the Nernst equation results in:

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log K
\]  
(4)

Which simplifies to \(E^\circ_{\text{cell}} - E^\circ_{\text{cell}} = 0\). This means that when the redox reaction reaches equilibrium, the cell potential will equal 0.

Before coming to lab, calculate the expected cell potential for the nonstandard conditions you will be doing in section IB.

Concentration Cells

As can be seen in examining the Nernst equation (equation 3), the cell potential depends on both the standard cell potential (the half-reactions) but also the concentrations of the reactants and products. You will explore this in sections IB-III by varying the concentrations of the half-cells. However, if the two half-reactions are the same, \(E^\circ_{\text{cell}}\) will be equal to zero (i.e., the two half-reactions have equal reaction potentials) and \(E_{\text{cell}}\) is zero under standard conditions. If the concentrations in the half-cells are different, this difference in concentration will result in a current flow because electrons will spontaneously flow from the half-cell with the lower concentration to that of the higher concentration to re-establish equilibrium. This is the concept that will be explored in section IV below.

Before coming to class, calculate the expected cell potential with the various concentrations to be utilized. Compare your results to that calculate values.

PROCEDURE:

Note: please read below for information on use of volumetric glassware and the digital voltmeter.

Preparation of Half-Cells

Solutions: You will need to prepare solutions for each of your half-cells. In electrochemistry, exact concentrations and solution purity are highly important as deviations in concentration or
added impurities will affect the measured voltage. As such, you are to clean and dry your glassware (there is no need to rigorously dry the volumetric flasks as you will be adding water to these) before use and will be using precise glassware for making your solutions. The solutions you will need to make are:

a. 1.0 M Mg(NO$_3$)$_2$,
b. 1.0 M Cu(NO$_3$)$_2$, and
c. 0.01 M AgNO$_3$ for the half-cells.

Before coming to lab, determine the mass of Mg(NO$_3$)$_2$, Cu(NO$_3$)$_2$, AgNO$_3$ and that you will need to make 100 mL of each solution.

Electrochemical cells: To prepare your first electrochemical cell, obtain two thoroughly cleaned and dry 100 mL beakers. Fill each beaker with the solutions listed below.

I. Mg/Cu Cell:
   A. Standard Conditions: Fill one beaker with your 1.0 M Mg(NO$_3$)$_2$ solution and the other with your 1.0 M Cu(NO$_3$)$_2$ solution. Make sure to clearly label your half-cells. Then place the ends of the salt bridge in each beaker (shown in Figure 1 above). Ensure that the ends of the salt bridge are below the solution surfaces.

Connect your anode to the black lead of the voltmeter and the cathode to the red lead and turn the dial to read the DC voltage. Immerse the metal electrode in the proper solution making sure to not get the voltmeter leads wet. Your instructor will show you how to best do this. You can begin reading the cell voltage and record this value in your notebook. Compare the voltage to the one you calculated before coming to class.

B. Nonstandard Conditions:
   1. You will now dilute your Mg half-cell to 0.1M (keeping the Cu half-cell the same) and again measure the voltage. To perform the dilution, remove 10mL (using the volumetric pipet) from your 1.0M Mg(NO$_3$)$_2$ solution and transfer to a 100mL volumetric flask. Fill the remaining volume with distilled water. Measure the voltage of this electrochemical cell. How does this voltage compare to the one you calculated and to the previous cell under standard conditions?
   2. Dilute the Mg half-cell to 0.01 M and read the voltage.
   3. Prepare a 0.1 M Cu(NO$_3$)$_2$ half-cell the by diluting the 1M solution (as you did in step 1), connect to half-cells containing 1M Mg(NO$_3$)$_2$, 0.1 M Mg(NO$_3$)$_2$, and 0.01 M Mg(NO$_3$)$_2$ as in step 1. You should have a total of 6 voltages at this point (1 for the standard conditions and 5 for the nonstandard conditions).

What effect does the dilutions have on the voltage? How does the voltage of the cell change when the concentrations are unequal? Relate this change in concentration to Le Chatelier’s principle.
II. **Mg/Ag cell:** Fabricate electrochemical cells using 0.01 M AgNO$_3$ and each of the three Mg(NO$_3$)$_2$ dilutions (1.0, 0.1, and 0.01M). This time, you will need to determine which half-cell is the anode and which is the cathode from the calculated standard electrode potentials. You should have three different voltage measurements from this experiment (the AgNO$_3$ cell stays the same concentration).

III. **Cu/Ag cell:** Perform the same experiment as above, but with the three Cu dilutions (1.0M, 0.1M, and 0.01M) as the other half-cell. Again, you will need to determine which half-cell is the anode and which is the cathode from the calculated standard electrode potentials.

IV. **Cu/Cu cell:** You should now have three Cu(NO$_3$)$_2$ solutions (1.0M, 0.1M, and 0.01M). Prepare one half-cell with the 1.0M Cu solution and the other with the 0.1M Cu solution. If you have prepared your solutions carefully, your voltage should match very well what was calculated for the concentration pre-lab exercise. Perform the same experiment with the 1.0M/0.01M pair.

Each group should still have at least 90 mL of their 1.0M Cu(NO$_3$)$_2$ left. As a last experiment, you will compare your 1.0M Cu solution to a neighboring group’s. One half-cell will be your 1.0M Cu solution and the other will be the other group’s 1.0M Cu solution. What is the voltage? Is it what you expect? Use the Nernst equation above to determine who has the more accurate solution concentration.

### Table 1: Standard reduction potentials:

<table>
<thead>
<tr>
<th>Reduction Half-Reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}_2$(aq) + 2H$^+$(aq) + 2e$^-$ → 2H$_2$O(l)</td>
<td>1.78</td>
</tr>
<tr>
<td>$\text{Au}^{3+}$(aq) + 3e$^-$ → Au(s)</td>
<td>1.50</td>
</tr>
<tr>
<td>$\text{O}_2$(g) + 4H$^+$(aq) + 4e$^-$ → 2H$_2$O(l)</td>
<td>1.23</td>
</tr>
<tr>
<td>$\text{NO}_3^-$(aq) + 4H$^+$(aq) + 3e$^-$ → NO(g) + 2H$_2$O(l)</td>
<td>0.96</td>
</tr>
<tr>
<td>$\text{Ag}^+$(aq) + e$^-$ → Ag(s)</td>
<td>0.80</td>
</tr>
<tr>
<td>Cu$^+$ (aq) + e$^-$ → Cu(s)</td>
<td>0.52</td>
</tr>
<tr>
<td>$\text{O}_2$(g) + 2H$_2$O(l) + 4e$^-$ → 4OH$^-$ (aq)</td>
<td>0.40</td>
</tr>
<tr>
<td>Cu$^{2+}$(aq) + 2e$^-$ → Cu(s)</td>
<td>0.34</td>
</tr>
<tr>
<td>Cu$^{2+}$(aq) + e$^-$ → Cu$^+$(aq)</td>
<td>0.16</td>
</tr>
<tr>
<td>2H$^+$(aq) + 2e$^-$ → H$_2$(g)</td>
<td>0</td>
</tr>
<tr>
<td>2H$_2$O(l) + 2e$^-$ → H$_2$(g) + 2OH$^-$ (aq)</td>
<td>-0.83</td>
</tr>
<tr>
<td>Mg$^{2+}$(aq) + 2e$^-$ → Mg(s)</td>
<td>-2.37</td>
</tr>
</tbody>
</table>
Volumetric Flask: A volumetric flask is glassware used to prepare a solution to a known volume and measure volumes much more precisely than beakers or flasks. When your solution is filled to this line, the volume is exactly the volume indicated on the side of the flask (100 mL with a maximum allowable error of 0.08 mL). To make your solution, obtain the proper mass of solute and add to the volumetric flask taking care to not lose any material. Slowly add your solvent until the meniscus is at the indicator line on the neck of the flask. To ensure thorough mixing, cap the flask tightly and invert several times (~50).

Volumetric Pipet: A volumetric pipet is glassware used to measure out a known volume of solution precisely. Make sure to check your volumetric pipet to ensure that it is clean and free of breaks. As with the burets you’ve been using this semester, it is a good idea to clean the pipet with distilled water, followed by rinsing with a small portion of the solution you will use to fill. There will be a small amount of liquid remaining in the tip, do not try to remove it. The pipet is calibrated to take into account the solution that remains at the tip. You will be using pipet pumps to draw up the solution. Place the pump on the top of the pipet and the pipet tip in your solution. Draw up the solution by rotating the thumb wheel, being careful to not draw up the solution too fast or you will get solution in the pump. Draw up the solution until the meniscus is at the calibration line. Remove the pipet from your solution and the solution transferred. This may require practice. You are encouraged to practice with distilled water first.

Digital Voltmeter: A voltmeter is a device used to measure potential differences between two points in an electrical circuit. As current flows through the high internal resistance voltmeter, a voltage is generated because of the direct relationship between voltage and current by Ohm’s Law (V = IR, where V is voltage, I is current, and R is the resistance of the voltmeter).