Electrochemistry

Objectives:
To use principles of electrochemistry to understand the properties of electrochemical cells and electrolysis.

Background:

Part I: Galvanic Cells:
A Galvanic cell is a device that spontaneously produces an electric current by coupling two oxidation-reduction half reactions. The basic set-up consists of two electrodes immersed in different electrolyte solutions separated by a salt bridge, or similar connection, that permits the flow of ions while keeping the two solutions separated.

Consider the oxidation-reduction reaction between lead and silver described by the equation:

\[ \text{Pb}(s) + 2\text{Ag}^{+}(aq) \rightarrow \text{Pb}^{2+}(aq) + 2\text{Ag}(s) \]

This equation can be separated into two half-reaction equations:

\[ \text{Pb}(s) \rightarrow \text{Pb}^{2+}(aq) + 2e^{-} \] (oxidation)

and

\[ 2\text{Ag}^{+}(aq) + 2e^{-} \rightarrow 2\text{Ag}(s) \] (reduction)

A Galvanic cell that uses these two half-reactions is illustrated below:
The salt bridge is required to complete the electrical connection. Positive Pb\(^{2+}\)(aq) ions are produced at the lead electrode. For each Pb\(^{2+}\)(aq) ion produced, two NO\(_3\)^{−}(aq) ions flow from the salt bridge into the Pb(NO\(_3\))\(_2\)(aq) solution to maintain electrical neutrality. Because of its charge, two positive Ag\(^{+}\) ions are consumed at the silver electrode for each Pb\(^{2+}\)(aq) ion produced. This in turn causes two K\(^{+}\)(aq) ions to flow simultaneously from the salt bridge into the silver nitrate solution. These ion flows maintain electrical neutrality in both the cell solutions and the salt bridge.

We can represent this cell in a compact form using a **cell diagram**:

\[
Pb(s) \mid Pb(NO_3)_2(aq) \parallel AgNO_3(aq) \mid Ag(s)
\]

In a cell diagram, the single vertical bars indicate boundaries of phases that are in contact, and the double vertical bars indicate a salt bridge. Thus, in the cell represented by this diagram, Pb(s) and Pb(NO\(_3\))\(_2\)(aq) are separate phases in physical contact, as are AgNO\(_3\)(aq) and Ag(s), and a salt bridge separates the Pb(NO\(_3\))\(_2\)(aq) and AgNO\(_3\)(aq) solutions. By convention, we write the metal electrodes at the ends of the diagram, insoluble substances and/or gases adjacent to the metals, and soluble species near the center of the diagram. The species that undergo oxidation are written on the left-hand side of the diagram, and those that undergo reduction are written on the right-hand side.

The **cell potential**, \(E_{\text{cell}}\), as measured in volts, is determined by the **Nernst Equation**,

\[
E_{\text{cell}} = E_{\text{cell}}^\circ - \left( \frac{RT}{\nu_e F} \right) \ln Q
\]

where \(R\) is the ideal gas constant, 8.3145 J·mol\(^{-1}\)·K\(^{-1}\), \(T\) is the temperature in Kelvin, \(\nu_e\) is the stoichiometric coefficient of the number of electrons transferred in the balanced half-reaction equations, \(F\) is the Faraday constant, 96,485 C·mol\(^{-1}\), and \(Q\) is the thermodynamic reaction quotient.

The value of the **standard cell potential**, \(E_{\text{cell}}^\circ\), is determined from the sum of the standard oxidation and reduction potentials of the two half-cell reactions,

\[
E_{\text{cell}}^\circ = E_{\text{red}}^\circ + E_{\text{ox}}^\circ
\]

**Table 1** lists standard reduction potentials, \(E_{\text{red}}^\circ\), for various half-cell reactions. Values for the standard oxidation potentials, \(E_{\text{ox}}^\circ\), are obtained by reversing the listed reduction reaction equations and their corresponding signs.
Table 1: Standard reduction potentials at 25.0°C for aqueous solutions*

<table>
<thead>
<tr>
<th>Electrode half reaction</th>
<th>$E^\circ_{\text{red/V}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acidic solutions</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{F}_2(g) + 2e^- \rightarrow 2\text{F}^-(aq)$</td>
<td>+2.87</td>
</tr>
<tr>
<td>$\text{O}_3(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{O}_2(g) + \text{H}_2\text{O}(l)$</td>
<td>+2.08</td>
</tr>
<tr>
<td>$\text{S}_2\text{O}_5^{2-}(aq) + 2e^- \rightarrow 2\text{SO}_4^{2-}(aq)$</td>
<td>+2.01</td>
</tr>
<tr>
<td>$\text{Co}^{3+}(aq) + e^- \rightarrow \text{Co}^{2+}(aq)$</td>
<td>+1.92</td>
</tr>
<tr>
<td>$\text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^-(aq)$</td>
<td>+1.36</td>
</tr>
<tr>
<td>$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$</td>
<td>+1.23</td>
</tr>
<tr>
<td>$\text{Pt}^{2+}(aq) + 2e^- \rightarrow \text{Pt}(s)$</td>
<td>+1.18</td>
</tr>
<tr>
<td>$\text{Br}_2(l) + 2e^- \rightarrow 2\text{Br}^-(aq)$</td>
<td>+1.07</td>
</tr>
<tr>
<td>$\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l)$</td>
<td>+0.96</td>
</tr>
<tr>
<td>$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$</td>
<td>+0.80</td>
</tr>
<tr>
<td>$\text{I}_2(s) + 2e^- \rightarrow 2\text{I}^-(aq)$</td>
<td>+0.54</td>
</tr>
<tr>
<td>$\text{Cu}^+(aq) + e^- \rightarrow \text{Cu}(s)$</td>
<td>+0.52</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$</td>
<td>+0.34</td>
</tr>
<tr>
<td>$\text{AgCl}(s) + e^- \rightarrow \text{Ag}(s) + \text{Cl}^-(aq)$</td>
<td>+0.22</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(aq) + e^- \rightarrow \text{Cu}^+(aq)$</td>
<td>+0.15</td>
</tr>
<tr>
<td>$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$</td>
<td>+0.0</td>
</tr>
<tr>
<td>$\text{Pb}^{2+}(aq) + 2e^- \rightarrow \text{Pb}(s)$</td>
<td>−0.13</td>
</tr>
<tr>
<td>$\text{V}^{3+}(aq) + e^- \rightarrow \text{V}^{2+}(aq)$</td>
<td>−0.26</td>
</tr>
<tr>
<td>$\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$</td>
<td>−0.26</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s)$</td>
<td>−0.45</td>
</tr>
<tr>
<td>$\text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s)$</td>
<td>−0.76</td>
</tr>
<tr>
<td>$\text{Mn}^{2+}(aq) + 2e^- \rightarrow \text{Mn}(s)$</td>
<td>−1.19</td>
</tr>
<tr>
<td>$\text{Al}^{3+}(aq) + 3e^- \rightarrow \text{Al}(s)$</td>
<td>−1.66</td>
</tr>
<tr>
<td>$\text{H}_2(g) + 2e^- \rightarrow 2\text{H}^+(aq)$</td>
<td>−2.23</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg}(s)$</td>
<td>−2.37</td>
</tr>
<tr>
<td>$\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s)$</td>
<td>−2.71</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}(aq) + 2e^- \rightarrow \text{Ca}(s)$</td>
<td>−2.87</td>
</tr>
<tr>
<td>$\text{K}^+(aq) + e^- \rightarrow \text{K}(s)$</td>
<td>−2.93</td>
</tr>
<tr>
<td>$\text{Li}^+(aq) + e^- \rightarrow \text{Li}(s)$</td>
<td>−3.04</td>
</tr>
<tr>
<td><strong>Basic solutions</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^-(aq)$</td>
<td>+0.40</td>
</tr>
<tr>
<td>$\text{Cu(OH)}_2(s) + 2e^- \rightarrow \text{Cu}(s) + 2\text{OH}^-(aq)$</td>
<td>−0.22</td>
</tr>
<tr>
<td>$\text{Fe(OH)}_3(s) + e^- \rightarrow \text{Fe(OH)}_2(s) + \text{OH}^-(aq)$</td>
<td>−0.56</td>
</tr>
<tr>
<td>$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$</td>
<td>−0.83</td>
</tr>
<tr>
<td>$2\text{SO}_4^{2-}(aq) + 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{S}_2\text{O}_4^{2-}(aq) + 4\text{OH}^-(aq)$</td>
<td>−1.12</td>
</tr>
</tbody>
</table>

For example, for the lead-silver cell described above, the value of the standard reduction potential for the silver half-reaction listed in Table 1 is $E_{\text{red}}^* = +0.80 \text{ V}$. The value of the standard oxidation potential for the lead half-reaction is found by reversing the reaction equation in the table and the sign of $E_{\text{red}}^*$ listed, to obtain $E_{\text{ox}}^* = +0.13 \text{ V}$. Thus, the standard cell potential for the lead-silver cell is,

$$E_{\text{cell}}^* = 0.13 \text{ V} + 0.80 \text{ V} = 0.93 \text{ V}$$

If the concentrations of the lead nitrate and silver nitrate solutions are values other than 1M, we can use the Nernst Equation to find the cell potential. For example, if the solutions used in the lead-silver cell are 0.1 M in Pb(NO$_3$)$_2$(aq) and 2.0 M in AgNO$_3$(aq) at 25°C, then the cell potential will be,

$$E_{\text{cell}} = E_{\text{cell}}^* - \frac{RT}{v_e F} \ln \left( \frac{[\text{Pb}^{2+}] / \text{M}}{[\text{Ag}^{+}] / \text{M}^2} \right)$$

$$= 0.93 \text{ V} - \frac{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})}{(2)(96485 \text{ C} \cdot \text{mol}^{-1})} \ln \left( \frac{0.1}{[2.0]^2} \right)$$

$$= 0.98 \text{ V}$$

A Nernst plot can be used to find the value of $E_{\text{cell}}^*$ and determine the concentration of a solution. To make a Nernst plot, we fix the concentration in one of our two half-cells, and vary the concentration in the other, plotting the cell potential as a function of the natural logarithm of the varying concentration. For example, if we fix the concentration of AgNO$_3$(aq) in our silver half-cell at 1.0 M, and allow the concentration of the lead(II) nitrate solution in our lead half-cell to vary, we obtain:

$$E_{\text{cell}} = -\frac{RT}{v_e F} \ln \left( \frac{[\text{Pb}^{2+}] / \text{M}}{[1.0]^2 / \text{M}^2} \right) + E_{\text{cell}}^*$$

where we have written the Nernst Equation in the form of the familiar $y=mx+b$ equation of a line. Thus, if we measure the cell potential for a series of lead(II) nitrate solutions of known concentration, and then plot the cell potential as a function of the natural logarithm of these concentrations, we obtain a line with a slope of $m = -RT/v_e F$ and an intercept of $b = E_{\text{cell}}^*$.

Once the equation of the line is determined, we can use it to find the concentration of an unknown lead nitrate solution from the measured cell potential of the solution paired with a standard half-cell.

In the first part of this experiment, we will make a standard zinc-copper cell. We will then use the half-cells to determine the identity of an unknown metal. Finally, we will measure the electric potentials of a series of zinc-copper cells, using these to construct a Nernst plot and determine the concentration of an unknown copper(II) sulfate solution.
Part II: Electrolytic Cells:

In contrast to a Galvanic cell, which spontaneously produces an electric current, an Electrolytic cell is an electrochemical cell in which an external electrical current is used to drive an otherwise non-spontaneous chemical reaction. In an electrolytic cell, two electrodes are inserted into the solution that is to undergo electrolysis. No salt bridge or other method of separating the half reactions is required, because the reaction is non-spontaneous.

In our experiment, we will insert two graphite electrodes into a U-tube containing the solution that is to undergo electrolysis. The electrolysis of a 1.0-molar copper(II) chloride solution, CuCl₂(aq), is illustrated here.

The passing of an electrical current through the solution causes the aqueous chloride ions to undergo oxidation to chlorine gas at the positive electrode, or anode, where oxidation occurs, as described by the equation:

\[ 2\text{Cl}^- (aq) \rightarrow \text{Cl}_2 (g) + 2e^- \text{ (oxidation, anode)} \quad E_{ox}^- = -1.36 \text{ V} \]

The production of chlorine is evidenced by the formation of yellow-green bubbles at this electrode. The careful smelling of the gas by cautiously wafting a small amount towards the nose and observing a smell similar to that of a swimming pool is confirmation of chlorine. Such a test should be carried out cautiously, because chlorine gas is a respiratory irritant that is toxic in large quantities.

Similarly, the aqueous copper ions undergo reduction to metallic copper at the negative electrode, or cathode, where reduction occurs, as described by the equation:

\[ \text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu} (s) \text{ (reduction, cathode)} \quad E_{red}^- = +0.34 \text{ V} \]

The production of copper is evidenced by the slow formation of an orange-colored metallic deposit on this electrode.

The potential required to carry out this process at standard conditions is:

\[ E_{rxn}^- = E_{ox}^- + E_{red}^- = (-1.36 \text{ V}) + (0.34 \text{ V}) = -1.02 \text{ V} \]

Here the negative sign indicates that the reaction is non-spontaneous, and so the necessary current must be provided from an external source, such as a power supply. This process requires a minimum of 1.02 volts under standard conditions. In practice, a greater potential is
required to overcome internal cell resistance and other factors. If a reaction produces a gas, such as hydrogen or chlorine, additional energy may be required to liberate the gas from the electrode. This additional potential is called an overpotential. In some cases, the additional potential required can be quite substantial. Overpotential values for the formation of hydrogen, oxygen, and chlorine gases on platinum and graphite electrodes are given in Table 2.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Hydrogen</th>
<th>Oxygen</th>
<th>Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>–0.16 V</td>
<td>–0.95 V</td>
<td>–0.10 V</td>
</tr>
<tr>
<td>Graphite</td>
<td>–0.62 V</td>
<td>–0.95 V</td>
<td>–0.12 V</td>
</tr>
</tbody>
</table>

Thus, if the reaction described above for the formation of chlorine gas and metallic copper is carried out on a platinum electrode at 1 bar and 25°C, then because the overpotential required to liberate chlorine gas from platinum is –0.10 volts, the minimum potential required to carry out the reaction is given by the sum of \( E^\circ_{\text{rxn}} \) and the overpotential, or

\[
E^\circ_{\text{rxn}} = \left( -1.02 \text{ V} \right) + \left( -0.10 \text{ V} \right) = -1.12 \text{ V}
\]

When our cell is not at standard conditions, we must use the Nernst equation to determine the potential required at each electrode. For example, for the 1.0-M CuCl\(_2\)(aq) solution described, each dissolved CuCl\(_2\) molecule produces two chloride ions, and so the Cl\(^-\) (aq) ion concentration is 2.0 molar. Thus, we must use the Nernst equation to determine the minimum potential required to liberate chlorine gas (not including the overpotential). For the half-reaction occurring at the anode at 25°C and 1.0 bar, this potential is given by,

\[
E_{\text{ox}}^\circ = E_{\text{ox}}^\circ - \left( \frac{RT}{F} \right) \ln \left( \frac{P_{\text{Cl}}/\text{bar}}{[\text{Cl}^-]^2/\text{M}^2} \right) \\
= -1.36 \text{ V} - \frac{8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 298 \text{ K}}{2 \cdot 96485 \text{ C} \cdot \text{mol}^{-1}} \ln \left( \frac{1.0}{[2.0]^2} \right) \\
= -1.34 \text{ V}
\]

In this case, the value is not significantly different from that required for a standard 1.0-molar chloride solution.

When considering what products are formed at each electrode, we also need to consider the possible electrolysis of the solvent, or any other species present in solution. Because the solutions we will use in this experiment are aqueous, we must also consider the possible electrolysis of water to form hydrogen and oxygen gases, according to the equation:

\[
2\text{H}_2\text{O}(l)_{\text{electrolysis}} \rightarrow \text{O}_2(g) + 2\text{H}_2(g)
\]
This process can be described by the two half-reaction equations:

\[
2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \quad \text{(oxidation)} \quad E^\circ_{\text{ox}} = -1.23 \text{ V}
\]

and

\[
4\text{H}^+(aq) + 4\text{e}^- \rightarrow 2 \text{H}_2(g) \quad \text{(reduction)} \quad E^\circ_{\text{red}} = 0 \text{ V}
\]

These potentials are for standard states, or a hydrogen ion concentration of 1.0 molar, which corresponds to an acidic solution. In pure water, the hydrogen ion concentration is \(1.0 \times 10^{-7}\) molar, and so we must use the Nernst equation to find the correct potentials. Taking the pressure as 1.0 bar and the temperature as 25°C, for the oxidation half-reaction we obtain,

\[
E_{\text{ox}} = E^\circ_{\text{ox}} - \frac{RT}{v_e F} \ln \left( \frac{P_{\text{O}_2} \cdot [\text{H}^+]^4}{\text{bar} \cdot \text{M}^4} \right)
= -1.23 \text{ V} - \frac{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})}{(4)(96485 \text{ C} \cdot \text{mol}^{-1})} \ln \left( \frac{1.0}{1.0 \times 10^{-7}} \right)^4
= -0.82 \text{ V}
\]

and for the reduction half-reaction,

\[
E_{\text{red}} = E^\circ_{\text{red}} - \frac{RT}{v_e F} \ln \left( \frac{P_{\text{O}_2}^2 / \text{bar}^2}{[\text{H}^+]^4 / \text{M}^4} \right)
= 0 \text{ V} - \frac{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})}{(4)(96485 \text{ C} \cdot \text{mol}^{-1})} \ln \left( \frac{(1.0)^2}{(1.0 \times 10^{-7})^4} \right)
= -0.41 \text{ V}
\]

Thus, for pure water at 1.0 bar and 25°C, we have:

\[
2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \quad \text{(oxidation)} \quad E_{\text{ox}} = -0.82 \text{ V}
\]

and

\[
4\text{H}^+(aq) + 4\text{e}^- \rightarrow 2 \text{H}_2(g) \quad \text{(reduction)} \quad E_{\text{red}} = -0.41 \text{ V}
\]

These values do not include the overpotentials, which depend upon the specific electrodes used.
Let us now compare the possible oxidation reactions that can occur in an aqueous 1.0-molar copper(II) chloride solution at the anode. Using the potentials that we previously calculated, we have:

\[
2\text{Cl}^- (aq) \rightarrow \text{Cl}_2 (g) + 2e^- \quad \text{(oxidation)} \quad E_{\text{ox}} = -1.34 \text{ V}
\]

or

\[
2\text{H}_2\text{O}(l) \rightarrow \text{O}_2 (g) + 4\text{H}^+ (aq) + 4e^- \quad \text{(oxidation)} \quad E_{\text{ox}} = -0.82 \text{ V}
\]

From these results, we might conclude that oxygen gas (rather than chlorine gas) is formed at the anode, because it requires the less negative potential. However, we would be forgetting to include the overpotentials for the formation of the two gases. Taking our electrode to be graphite, and adding in the overpotentials for the formation of chlorine and oxygen gases listed in Table 2, we obtain:

**Possible oxidation reactions on a graphite anode for a 1.0-M CuCl}_2(aq) solution:**

\[
2\text{Cl}^- (aq) \rightarrow \text{Cl}_2 (g) + 2e^- \quad \text{(oxidation)} \quad E_{\text{ox}} = -1.46 \text{ V}
\]

or

\[
2\text{H}_2\text{O}(l) \rightarrow \text{O}_2 (g) + 4\text{H}^+ (aq) + 4e^- \quad \text{(oxidation)} \quad E_{\text{ox}} = -1.77 \text{ V}
\]

Thus, after accounting for the overpotentials, we find that chlorine gas is the one more easily evolved, in accord with what is observed experimentally.

Now let’s turn our attention to the possible reduction reactions that can occur at the cathode for our 1.0-molar aqueous copper(II) chloride solution. Using the potentials that we previously calculated, and including the overpotential for the formation of hydrogen gas on graphite, we have:

**Possible reduction reactions on a graphite cathode for a 1.0-M CuCl}_2(aq) solution:**

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

or

\[
4\text{H}^+ (aq) + 4e^- \rightarrow 2 \text{H}_2 (g) \quad \text{(reduction)} \quad E_{\text{red}} = -1.03 \text{ V}
\]

Here we find that the production of copper metal is favored, because it has a positive reduction potential, in comparison to that for the formation of hydrogen gas, which is negative.

Thus, we find that in our electrolytic cell, chlorine gas is produced at the anode, and copper metal is produced at the cathode, which is in accord with experimental observations.
Notice that even though the formation of copper metal has a positive reduction potential, the overall reaction is non-spontaneous because the total minimum potential required for the production of copper metal and chlorine gas under these conditions is:

\[ E_{\text{run}} = E_{\text{ox}} + E_{\text{red}} = (-1.46 \, \text{V}) + (0.34 \, \text{V}) = -1.12 \, \text{V} \]

Applying these principles, we can predict the reactions that occur in electrolytic cells and the minimum potentials required to carry them out.

In the second half of this experiment, we will construct a series of electrolytic cells, and determine the reactions occurring at the anode and cathode based on observation and theory. We will then identify an unknown.

**Procedure:**

**Materials and Equipment:**

You will need the following additional items for this experiment:

- ring stand
- voltmeter
- salt bridge
- copper and zinc metal electrodes
- two graphite electrodes
- 1.00-mL volumetric pipet
- 100.00-mL volumetric flask
- rubber pipet bulb
- glass u-tube
- power supply
- two red and black banana-alligator leads

**GENERAL SAFETY:** Students must wear safety goggles, coats, and gloves at all times.

**SMELLING OF CHEMICALS:** Chlorine and other gases that may be evolved during this experiment are known irritants and can be toxic at large concentrations. The smelling of evolved gases should be done cautiously, by wafting small quantities of the gases towards your nose. In no cases should you place your nose directly over the apparatus.

**WASTE DISPOSAL:** All used chemicals must be placed in the proper waste container.
Experimental Set-up and Procedure:

Part I, Galvanic Cells:

**Construct a Standard 1.0-M Zinc – 1.0-M Copper Galvanic Cell:**

Prepare a 1.0-M standard zinc half-cell by pouring approximately 20 mL of 1.0-M zinc chloride solution into a clean 50-mL beaker and inserting a clean dry zinc-metal electrode.

Prepare a 1.0-M standard copper half-cell by pouring approximately 20 mL of 1.0-M copper(II) sulfate solution into a second 50-mL beaker and inserting a clean dry copper-metal electrode.

Rinse the ends of your salt bridge. Insert one end into each of the two half-cells you prepared.

Insert the red and black wire leads that came with your voltmeter (*not the alligator leads for the power supply which may damage the meter*), and set the meter to 20 volts DC. Using your voltmeter, measure the cell potential and record this value.

Do not discard these half-cell solutions, as you will need them in later steps.

Using the data in Table 1, calculate the theoretical cell potential and determine your percentage error.

**Determining an Unknown Half-Cell:**

Your instructor will give you a metal and a 1.0-M solution containing ions of that metal labeled Unknown A, which can be used to form one of the following half-cells:

\[
\text{Ag}^+ | \text{Ag} \quad \text{Pb}^{2+} | \text{Pb} \quad \text{Fe}^{2+} | \text{Fe} \quad \text{Al}^{3+} | \text{Al} \quad \text{Mg}^{2+} | \text{Mg} \quad \text{Ni}^{2+} | \text{Ni}
\]

Construct a half-cell from this unknown metal and solution. Compare its potential to both the 1.0-M standard zinc and 1.0-M standard copper half-cells you constructed earlier. Determine the identity of Unknown A.

**Using a Nernst Plot to Determine Concentration:**

Starting with your 1.0-M copper(II) sulfate solution, and using a 1.00-mL volumetric pipet and a 100.00-mL volumetric flask, make a series of dilutions to prepare three half-cells containing approximately 20-mL of 1.0x10^-2 M, 1.0x10^-4 M, and 1.0x10^-6 M solutions of copper(II) sulfate.

Using your 1.0-M standard zinc half-cell, measure and record the cell potential of each of these three zinc-copper cells. Be sure to rinse and dry the copper-metal electrode and salt bridge between each trial.

Using Excel, construct a Nernst plot by plotting the potential you measured as a function of the natural logarithm of the concentration of copper ions in each of these cells. Find the equation of the best-fit trendline to these data. Include this plot with your report.

Unknown B contains a copper(II) nitrate solution of unknown concentration. Prepare a half-cell containing the solution in Unknown B. Using your standard 1.0-M zinc half-cell, measure and record the cell potential. From the equation of your Nernst plot, determine the concentration of copper ions in the unknown.
Part II, Electrolysis:

Determining Half-Cell Equations:
Using a utility clamp, connect a clean glass U-tube to your ring-stand. Fasten it such that the two open ends of the tube face upward, and the utility clamp is fastened about half-way down one side of the U-tube.
Fill the U-tube with a 0.1-M potassium iodide, KI (aq), solution, so that both ends of the tube are about half full.
Make certain the Power Supply is off.
Using the 0-20 volt setting on your Power Supply (the center two connectors), insert the two banana-clip ends of your banana-alligator leads into the Power Supply.
Gently connect the alligator clips at the other end of the leads to the end of your graphite electrodes, being careful not to break the electrodes. Insert one electrode into each end of your U-tube. Each electrode should extend part way into the solution.
Turn on the Power Supply and adjust the voltage to between 10 and 15 volts. Observe the reactions occurring at each electrode. Look for bubbles, plating out of metals, and color changes as evidence of a reaction.
If you observe bubbles, cautiously waft a small amount of the gas towards your nose and note any smell. Never place your nose directly above the tube. 
Add 2 drops of phenolphthalein indicator to each end of the U-tube, and observe any changes.
Add 2 drops of starch indicator to each end of the U-tube, and observe any changes.
Shut off the Power Supply.
Rinse out the glass U-tube, and rinse off the graphite electrodes, disposing properly of all chemicals.
Repeat this procedure using each of the following 0.1-M solutions: CuCl₂ (aq), Zn(NO₃)₂ (aq), Na₂SO₄ (aq), Ni(NO₃)₂ (aq), and NaBr (aq).
Record your observations and the half-reaction equations you believe are occurring at the anode and cathode for each of these six electrolytic cells.

Identifying an Unknown:
Unknown C contains one of the following aqueous solutions:

CuBr₂, ZnCl₂, NaI, NiCl₂, NaNO₃, ZnSO₄, KBr, ZnBr₂, NiBr₂, Nil₂, CuI₂, or CuSO₄

Proceeding in a similar manner, construct an electrolytic cell using Unknown C. Determine the half-reaction equations occurring at the anode and cathode, and the identity of the solution in Unknown C.
Team Name: ___________________________ Date: ______________________
Members: ___________________________ Lab Section: ________________

Electrochemistry

Part I, Galvanic Cells:

Standard 1.0-M Zinc – 1.0-M Copper cell:

Write the half-cell and overall net ionic equation for the oxidation-reduction reaction occurring in this cell. List the standard potential for each reaction equation as written:

<table>
<thead>
<tr>
<th>Reaction Equation</th>
<th>Half-Cell Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc half-cell reaction equation:</td>
<td></td>
</tr>
<tr>
<td>Copper half-cell reaction equation:</td>
<td></td>
</tr>
<tr>
<td>Net ionic reaction equation:</td>
<td>$E^{\circ}_{\text{cell}}$ (theoretical):</td>
</tr>
</tbody>
</table>

Measured value of $E^{\circ}_{\text{cell}}$: ________________ Percentage Error: _____________

Determining an Unknown 1.0-M Half-Cell:

Unknown Number: ___________-A

Measured value of $E_{\text{cell}}$ with 1.0-M zinc half-cell: ________________

Measured value of $E_{\text{cell}}$ with 1.0-M copper half-cell: ________________

Identity of metal in Unknown 1.0-M half-cell: ________________

Your unknown can be one of the following half-cells:

$\text{Ag}^{+}|\text{Ag} \quad \text{Pb}^{2+}|\text{Pb} \quad \text{Fe}^{2+}|\text{Fe} \quad \text{Al}^{3+}|\text{Al} \quad \text{Mg}^{2+}|\text{Mg} \quad \text{Ni}^{2+}|\text{Ni}$

Attach a separate sheet of paper detailing how you identified the half-cell in Unknown A. Be sure to include all supporting calculations.
Using a Nernst Plot to Determine Concentration:

Record the data for your three zinc-copper galvanic cells. The data for the 1.0-M copper half-cell is the same as that measured above in the first part of the experiment.

<table>
<thead>
<tr>
<th>[Cu^{2+}]:</th>
<th>1.0 M (from before)</th>
<th>1.0x10^{-2} M</th>
<th>1.0x10^{-4} M</th>
<th>1.0x10^{-6} M</th>
</tr>
</thead>
<tbody>
<tr>
<td>ln ([Cu^{2+}]/M):</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_{\text{cell Measured}} ):</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Using Excel, construct a Nernst plot by plotting the potential you measured as a function of the natural logarithm of the concentration of copper ions in each of these cells. Find the equation of the best-fit trendline to these data. **Include this plot with your report.**

Equation of Best-Fit Trendline to Plot: ________________________________

Value of \( E^{\circ}_{\text{cell}} \) from intercept: ________________ Percentage Error: _____________

Unknown Number: __________B Measured value of \( E_{\text{cell}} \) with Unknown: __________

Using your Nernst plot, determine the concentration of Unknown B. Show all work below:

Concentration of Unknown: ________________
Part II, Electrolysis:

Determining Half-Cell Equations:

0.1-M KI (aq) solution:

<table>
<thead>
<tr>
<th>Anode:</th>
<th>Cathode:</th>
</tr>
</thead>
<tbody>
<tr>
<td>observations:</td>
<td>observations:</td>
</tr>
<tr>
<td>Half-Reaction Equation:</td>
<td>Half-Reaction Equation:</td>
</tr>
</tbody>
</table>

0.1-M CuCl₂ (aq) solution:

<table>
<thead>
<tr>
<th>Anode:</th>
<th>Cathode:</th>
</tr>
</thead>
<tbody>
<tr>
<td>observations:</td>
<td>observations:</td>
</tr>
<tr>
<td>Half-Reaction Equation:</td>
<td>Half-Reaction Equation:</td>
</tr>
</tbody>
</table>

0.1-M Zn(NO₃)₂ (aq) solution:

<table>
<thead>
<tr>
<th>Anode:</th>
<th>Cathode:</th>
</tr>
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<tbody>
<tr>
<td>observations:</td>
<td>observations:</td>
</tr>
<tr>
<td>Half-Reaction Equation:</td>
<td>Half-Reaction Equation:</td>
</tr>
</tbody>
</table>
### 0.1-M Na₂SO₄ (aq) solution:

<table>
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<tr>
<th>Anode:</th>
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<tbody>
<tr>
<td>observations:</td>
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</tr>
</tbody>
</table>

Half-Reaction Equation:

<table>
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<tr>
<th>Anode:</th>
<th>Cathode:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 0.1-M Ni(NO₃)₂ (aq) solution:

<table>
<thead>
<tr>
<th>Anode:</th>
<th>Cathode:</th>
</tr>
</thead>
<tbody>
<tr>
<td>observations:</td>
<td>observations:</td>
</tr>
</tbody>
</table>

Half-Reaction Equation:

<table>
<thead>
<tr>
<th>Anode:</th>
<th>Cathode:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 0.1-M NaBr (aq) solution:

<table>
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<tr>
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<th>Cathode:</th>
</tr>
</thead>
<tbody>
<tr>
<td>observations:</td>
<td>observations:</td>
</tr>
</tbody>
</table>

Half-Reaction Equation:

<table>
<thead>
<tr>
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<th>Cathode:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Identifying an Unknown:

Unknown C contains one of the following aqueous solutions:

\[
\text{CuBr}_2, \text{ZnCl}_2, \text{NaI}, \text{NiCl}_2, \text{NaNO}_3, \text{ZnSO}_4, \text{KBr}, \text{ZnBr}_2, \text{NiBr}_2, \text{NiI}_2, \text{CuI}_2, \text{or CuSO}_4,
\]

Record your observations in the table below and use them to identify the unknown.

<table>
<thead>
<tr>
<th>Anode:</th>
<th>Cathode:</th>
</tr>
</thead>
<tbody>
<tr>
<td>observations:</td>
<td>observations:</td>
</tr>
<tr>
<td>Half- Reaction Equation:</td>
<td>Half- Reaction Equation:</td>
</tr>
</tbody>
</table>

Unknown Solution Number: _______ -C   Identity: ________________

Questions:

Attach your answers on a separate sheet of paper. Show all supporting work.

1. In your galvanic cells in Part I, was the anode positive or negative? Was this also the case in your electrolytic cells in Part II? Explain why or why not.

2. The slope of your Nernst plot is equal to: \( m = \frac{RT}{nF} \). Assuming a temperature of 20°C, use your slope to find the experimentally determined value of the Faraday Constant, \( F \). Calculate the percentage error in your determination.

3. An electrolytic cell contains a 0.1-M PbBr\(_2\) (aq) solution. Using Table 1, list all possible half-reaction equations for the anode and cathode of this cell. Hint: Recall that the solvent for this reaction is water.

4. Using the Nernst Equation and the overpotentials on graphite listed in Table 2, predict which of the half-reaction equations you listed for Question 3 occurs at the anode and cathode at 25°C and 1.0 bar. Show all work and justify your answers.

5. If a current of 0.50 Amperes is passed for 10 minutes through the 0.1-M PbBr\(_2\) (aq) cell described in Question 3, determine the mass of each of the products formed at the two electrodes. Assume that the concentrations of the various species present in the cell do not change appreciably over this time.

6. If a chemist wanted to make sodium metal by the electrolysis of seawater, what challenges would she face? How might she overcome these and achieve this goal?