Galvanic Cells and the Nernst Equation

ename:___________________________

Laboratory Section: _______

Galvanic Cells and the Nernst Equation

Equipment

- Voltage probe wires
- 0.1 M solutions of Pb(NO₃)₂, Fe(NO₃)₃, and KNO₃
- sandpaper or steel wool
- 0.1 M solutions of Cu(NO₃)₂ and Zn(NO₃)₂
- plastic document protector
- 1.0 M solutions of Cu(NO₃)₂ and Zn(NO₃)₂
- 6 x 1.5 cm strips of filter paper
- Cu(NO₃)₂: 0.010 M, 0.0010 M, and 0.00010 M

Objectives.

The objectives of this experiment are to develop an understanding of the "Electrochemical Series" and to illustrate the use the Nernst Equation.

Background

Any chemical reaction involving the transfer of electrons from one substance to another is an oxidation-reduction (redox) reaction. The substance losing electrons is oxidized while the substance gaining electrons is reduced. Let us consider the following redox reaction:

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

This redox reaction can be divided into an oxidation and a reduction **half-reaction.**

\[ \text{Zn(s)} \rightarrow \text{Zn}^{2+} \text{(aq)} + 2 \text{e}^{-} \quad \text{oxidation half-reaction} \]

\[ \text{Pb}^{2+} \text{(aq)} + 2 \text{e}^{-} \rightarrow \text{Pb(s)} \quad \text{reduction half-reaction} \]

A **galvanic cell** (Figure 1.) is a device used to separate a redox reaction into its two component half-reactions in such a way that the electrons are forced to travel through an external circuit rather than by direct contact of the oxidizing agent and reducing agent. This transfer of electrons through an external circuit is electricity.

Figure 1.
Each side of the galvanic cell is known as a **half-cell**. For the redox reaction above, each half-cell consists of an electrode (the metal of the half-reaction) and a solution containing the corresponding cation of the half-reaction.

The electrodes of the half-cells are connected by a wire through which the electrons can flow. In the cell, oxidation takes place at the zinc electrode, liberating electrons to the external circuit. Reduction takes place at the lead electrode, consuming electrons coming from the external circuit.

- **The electrode at which oxidation occurs is called the anode.**
- **The electrode at which reduction occurs is called the cathode.**

Since *oxidation releases electrons to the anode*, it is designated the **negative electrode** in the galvanic cell.

*Reduction removes the electrons from the cathode*: it is the **positive electrode**. As zinc atoms are oxidized, the excess positive charge \((\text{Zn}^{2+}\text{ ions})\) accumulates in solution around the zinc anode.

Likewise, excess negative charge \((\text{NO}_3^{-1}\text{ ions})\) accumulates around the lead cathode as \(\text{Pb}^{2+}\text{ ions}\) are removed from the solution of \(\text{Pb(NO}_3\text{)}_2\) by reduction of the lead metal.

These excess charges create an electric field that causes the ions to migrate: **positive ions (cations) migrate toward the cathode and negative ions (anions) migrate toward the anode.** In order to make this flow of ions between the two half-cells possible, the cells are connected by a porous barrier (or **salt bridge**) through which the ions can flow. The barrier prevents free mixing of the two solutions but permits limited movement of ions so that the "electrical neutrality" is maintained in each half-cell.

Different metals, such as zinc and lead, have different tendencies to oxidize; similarly, their ions have different tendencies to undergo reduction. The cell "potential" of a galvanic cell is due to the difference in tendencies of the two metals to oxidize (lose electrons) or their ions to reduce (gain electrons). Commonly, a **reduction potential**, a tendency to gain electrons, is used to represent the relative tendency for a given metal ion to undergo reduction.

The voltage measured in the cell is the result of the two half-reactions, and the magnitude of the potential (voltage) depends on the concentrations of the ions, the temperature, and pressure of gases.

When all the concentrations of the zinc/lead system are 1.0 M and the temperature is 25°C, the cell voltage is 0.63 volts. It would be a monumental task to assemble a list of all the possible cells and report their voltage. Instead we use the potential voltage of the half-reactions.

We cannot measure any half-cell potential directly (since it must be coupled with an opposing half-cell) so, we pick one half-reaction, call it the standard, construct a cell, measure the cell voltage and report the potential **relative to the standard**.
The standard that has been chosen by convention is:

\[ 2 \text{H}^{+} + 2 \text{e}^{-} \rightarrow \text{H}_2(g) \quad E^\circ = 0.00 \text{ volts} \]

Here the notation \( E^\circ \) is called the standard electrode potential and is the assigned potential of the standard hydrogen electrode when the concentration of \( \text{H}^+ \) is 1.0 M and the pressure of the hydrogen gas is 1.0 atmosphere. The measured cell voltage using the standard hydrogen electrode is therefore the potential of the other half-reaction.

Tables of standard half-reactions potentials have been computed. The reactions by convention are written as reductions and consequently the tables are of "Standard Reduction Potentials". A brief example follows.

<table>
<thead>
<tr>
<th>Half-reaction Potential (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}^{2+} + 2 \text{e}^{-} \rightarrow \text{Cu(s)} )</td>
</tr>
<tr>
<td>( 2 \text{H}^+ + 2 \text{e}^{-} \rightarrow \text{H}_2(g) )</td>
</tr>
<tr>
<td>( \text{Pb}^{2+} + 2 \text{e}^{-} \rightarrow \text{Pb(s)} )</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} + 2 \text{e}^{-} \rightarrow \text{Zn(s)} )</td>
</tr>
<tr>
<td>( \text{Mg}^{2+} + 2 \text{e}^{-} \rightarrow \text{Mg(s)} )</td>
</tr>
<tr>
<td>( \text{Li}^{+} + \text{e}^{-} \rightarrow \text{Li(s)} )</td>
</tr>
</tbody>
</table>

The greater the tendency of the ion to gain electrons and undergo reduction, the less negative (or more positive) the reduction potential of the ion. In the zinc/lead cell, the lead has a greater tendency to undergo reduction than the zinc.

In the zinc/lead cell, the measured potential of 0.63 volts can be deduced from the sum of the potentials of the two half-reactions.

\[
\begin{align*}
\text{Zn(s)} & \rightarrow \text{Zn}^{2+} + 2 \text{e}^{-} \quad +0.76 \text{ v} \\
\text{Pb}^{2+} + 2 \text{e}^{-} & \rightarrow \text{Pb(s)} \quad -0.13 \text{ v} \\
\text{Zn(s)} + \text{Pb}^{2+} & \rightarrow \text{Zn}^{2+} + \text{Pb(s)} \quad +0.63 \text{ v}
\end{align*}
\]

**NOTE:** The sign of the standard reduction potential for the zinc half-reaction is reversed to find the potential of the oxidation half-reaction.

In Part I of this experiment, other metal/ion half-cells will be tried. From the data, a table will be developed, listing various elements and ions in order of their tendency to gain or lose electrons.
The Nernst Equation

Theoretical predictions of "tendency to gain electrons" are used to predict the voltage difference between two electrodes. The voltage difference between electrodes, the cell voltage, is also called the Electromotive Force, or emf (E or E\text{\text{cell}}). Under standard conditions (25°C, 1.0 M solution concentrations, 1.0 atm gas pressures), these theoretically predicted voltages are known as standard emf's (E\text{\text{\text{o}}} or E\text{\text{\text{o}}}_\text{cell}).

In reality, standard conditions are often difficult if not impossible to obtain. The Nernst Equation allows cell voltages to be predicted when the conditions are not standard. Walter Nernst developed the following equation in the late 1800's while studying the thermodynamics of electrolyte solutions:

\[ \xi\text{cell} = \xi\text{cell}^0 - \frac{2.303RT}{nF} \log Q \]  

In equation (1), R is the gas constant, 8.314 J/mol-K, T is the temperature in Kelvin, F is Faraday's constant (96,485 coulombs/mol), n is the number of electrons transferred in the balanced oxidation/reduction reaction, and Q is the reaction quotient ([products]/[reactants]).

If the reactions are carried out at room temperature, 25°C, the Nernst equation becomes

\[ \xi\text{cell} = \xi\text{cell}^0 - \frac{0.0591}{n} \log Q \]  

Note in equations (1) and (2) that if all concentrations are 1.0 M, then Q would be equal to 1 and \( E\text{cell} = E\text{cell}^0 \).

In part II of this experiment, voltages will be measured at various concentrations for the zinc/copper galvanic cell and compared with those calculated using the Nernst Equation. This data will be used to determine the concentration of an unknown copper solution.

---

Safety Precautions

Safety goggles must be worn in the lab at all times. Any skin contacted by chemicals should be washed immediately.
Part I: Galvanic Cells

In this experiment, you will develop a simple version of the galvanic cell. As shown in Figure 2, a galvanic cell can be made with a strip of filter paper and small squares of metal. The filter paper provides the "reservoir" for the metal ion solutions and acts as the salt bridge.

![Figure 2. Galvanic Cell Setup](image)

The small squares of metal will be the electrodes of the galvanic cells. Notice that each strip of filter paper has a piece of lead on one end. The lead will be the reference electrode, and will be assigned a voltage of zero. We will measure all cell voltages relative to the reduction of lead:

\[
Pb^{2+}_{(aq)} + 2 \, e^{-} \rightarrow Pb_{(s)} \quad E^o = 0.00 \text{ Volts}
\]

![Figure 3. Filter Paper Galvanic Cells](image)
Procedure

1. Place three strips of filter paper (6 x 1.5 cm) about 4 cm apart on a plastic document protector.

2. Obtain the following squares of metal: 3 strips of lead (Pb), 1 strip of copper (Cu), 1 strip of zinc (Zn), and 1 strip of iron (Fe).

3. Lightly sand or steel wool one side of each of the metal squares and place them on one end of the filter paper strips as shown in Figure 3.

4. Place the following solutions under the corresponding square of metal:
   a) 2 drops of 0.10 M Pb(NO$_3$)$_2$ under each lead square,
   b) 2 drops of 0.10 M Cu(NO$_3$)$_2$ under the copper square,
   c) 2 drops of 0.10 M Zn(NO$_3$)$_2$ under the zinc square,
   d) 2 drops of 0.10 M Fe(NO$_3$)$_3$ under the iron square.

   **NOTE:** These drops provide the metal ion solutions for the electrochemical reactions.

5. Place 2-5 drops of 0.10 M KNO$_3$ in the center of each strip of filter paper, ensuring that the KNO$_3$ and the solutions under each metal come in contact with each other. The KNO$_3$ on the filter paper is acting as the salt bridge.

6. Connect two voltage probes to the LabWorks interface; the red voltage probe to the "V" input (red post) and the black voltage probe to the ground (violet post). **Note:** Alligator clips with short metal leads inserted are recommended for probes.

7. From the LabWorks window, click the **Design** button on the toolbar and choose the **EZ Program** option button.

8. Drop the menu choices for the "Read" window in line (3.). Select **Time** as you input and "time" as your label.

9. Drop the menu choices for the "Read" window in line (4.) and select "V" as your input choice. The computer will automatically label this input as "V".

10. Set the **delay** in line (6.) for 2 seconds. Select the **Acquire** button on the toolbar, and click the **Start** button to begin the program.

11. Starting with the Pb/Cu combination, measure the voltages produced from the filter-paper galvanic cells with the wires attached to the "V" input of the interface. Touch the metal probes in the alligator clips to the metal strips on the filter paper, as shown in Figure 2. Continue to take data until the voltage of the cell stabilizes in the spreadsheet. **Record the voltage (in millivolts) on your Report Sheet.**

   **Note:** You will need a firm contact with the metal, so press fairly hard. Do not allow the leads to come in contact with the solutions. Position the probes so that you get a positive voltage for the Pb/Cu system, that is, **the Lead is always the ground.**

12. Repeat step 11 for the Pb/Zn system and the Pb/Fe system.
13. Build a copper-zinc cell, measure its voltage and **record the value on your Report Sheet. (with the zinc as the ground)**

14. Click the Stop button in the lower left of the screen. There is no need to save the data.

15. The pieces of filter paper can be thrown away. Save the metal strips after rinsing thoroughly. Wash the document protector with distilled water and dry.

**Part II: The Nernst Equation**

In this experiment, you will examine the effect of solution concentration on the cell voltage for the reaction:

\[
\text{Cu}^{2+} \text{(aq)} + \text{Zn} \rightarrow \text{Cu} \text{(s)} + \text{Zn}^{2+} \text{(aq)}
\]

The Nernst equation allows you to calculate the \(E_{\text{cell}}\) as a function of the reactant and product concentrations. For the above reaction at 25°C, the Nernst equation becomes:

\[
E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \left( \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)
\]

Remember, solids and pure liquids are not included in the "Q" expression. Theoretically, \(E_{\text{cell}}^0\) for the above reaction is **1.10 volts**. Thus a value of \(E_{\text{cell}}\) can be calculated, knowing \([\text{Zn}^{2+}]\) and \([\text{Cu}^{2+}]\).

**Procedure**

1. Obtain six squares of zinc and six squares of copper and lightly sand or steel wool one side of each square.

2. Lay out six strips of filter paper (6 x 1.5 cm) on the document protector as in Part I.

3. Place the zinc and copper squares on the opposite ends of the strips of filter paper.

4. Place 2 drops of the following \(\text{Zn}^{2+}\) and \(\text{Cu}^{2+}\) solution concentrations under the zinc and copper squares respectively. Again, place 2-5 drops of the 0.10 M KNO\(_3\) solution between the two metal squares in each cell.

<table>
<thead>
<tr>
<th>Cell #</th>
<th>([\text{Cu}^{2+}])</th>
<th>([\text{Zn}^{2+}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0 M</td>
<td>1.0 M</td>
</tr>
<tr>
<td>2</td>
<td>0.10 M</td>
<td>1.0 M</td>
</tr>
<tr>
<td>3</td>
<td>0.010 M</td>
<td>1.0 M</td>
</tr>
<tr>
<td>4</td>
<td>0.0010M</td>
<td>1.0 M</td>
</tr>
<tr>
<td>5</td>
<td>0.00010 M</td>
<td>1.0 M</td>
</tr>
<tr>
<td>6</td>
<td>unknown</td>
<td>1.0 M</td>
</tr>
</tbody>
</table>
5. Measure the voltage ($E_{cell}$) for each of the half-cell combinations and **record these voltages** (in volts this time) on your **Report Sheet in Column E.** (Remember: zinc is the ground)

6. Click **Analyze** and select **Create a New File.** Manually input the copper and zinc concentrations of the **first five cells only** in Columns A and B, respectively.

7. Highlight Column C and use **Column Setup** to calculate the ratio, $[\text{Zn}^{2+}] / [\text{Cu}^{2+}]$.

8. Highlight Column D and use **Column Setup** to calculate the $\log([\text{Zn}^{2+}] / [\text{Cu}^{2+}])$.

9. Input your measured voltages for each of the cells in **Column E.**

10. Highlight Column F and use **Column Setup** and the Nernst Equation to find the calculated theoretical values for the voltages, $E_{cell}$, of each cell. e.g. $1.10 - ((0.0591/2) \times (D))$

11. With this data, select **Graph Setup** from the Menu bar and construct a plot of $E_{cell}$ (measured) vs. $\log([\text{Zn}^{2+}] / [\text{Cu}^{2+}])$. That is, Column E vs Column D ($E_{cell}$ (measured) on the y-axis and $\log([\text{Zn}^{2+}] / [\text{Cu}^{2+}])$ on the x-axis)

12. Make a linear regression plot for the data and obtain a printout to attach to your Report Sheet.

13. **Using the equation obtained from the linear regression (at the top of your graph)** calculate the concentration of the Unknown copper solution using its cell voltage. **Record this concentration on your Report Sheet.**

14. Save the metal squares after rinsing with distilled water. Discard the filter paper strips.
Part I: Galvanic Cells

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Cell Voltage compared to Pb^{2+}/Pb^{0} half-cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}^{2+} + 2 \text{e}^{-} \rightarrow \text{Cu}^{(s)} )</td>
<td>mV</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} + 2 \text{e}^{-} \rightarrow \text{Zn}^{(s)} )</td>
<td>mV</td>
</tr>
<tr>
<td>( \text{Pb}^{2+} + 2 \text{e}^{-} \rightarrow \text{Pb}^{(s)} )</td>
<td>mV</td>
</tr>
<tr>
<td>( \text{Fe}^{2+} + 2 \text{e}^{-} \rightarrow \text{Fe}^{(s)} )</td>
<td>mV</td>
</tr>
</tbody>
</table>

1. According to your table, which half-cell reaction has the greatest tendency toward reduction; that is, to gain electrons?

Which half-cell has the greatest tendency toward oxidation?

2. Based on your electrochemical series table, what would you predict for the voltage of a copper/zinc cell? Show your calculation.

3. What voltage did you actually record for your copper/zinc cell?
Part II: The Nernst Equation

<table>
<thead>
<tr>
<th>Column A</th>
<th>Column B</th>
<th>Column C</th>
<th>Column D</th>
<th>Column E</th>
<th>Column F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M</td>
<td>1.0 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10 M</td>
<td>1.0 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.010 M</td>
<td>1.0 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0010 M</td>
<td>1.0 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00010 M</td>
<td>1.0 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Do Not Enter The Unknown Voltage Into The Spreadsheet. It will be used below. Simply enter the voltage value for your unknown in the space provided here.

<table>
<thead>
<tr>
<th>Unknown</th>
<th>1.0 M</th>
</tr>
</thead>
</table>

1. How do the measured and calculated values for $E_{\text{cell}}$ compare? If they differ significantly, can you offer any explanation for the difference? (Hint: Since there is electrical resistance across the cells, what does Ohm's Law, $E = I \cdot R$, tell you......$E$ is voltage, $I$ is current and $R$ is resistance.)

2. Using the equation you obtained for the linear regression of $E_{\text{cell}}$ vs. log($[\text{Zn}^{2+}] / [\text{Cu}^{2+}]$), calculate the concentration of the unknown copper solution using its cell voltage. Show your work below.

3. What is the value of the slope in your linear regression of $E_{\text{cell}}$ vs. log($[\text{Zn}^{2+}] / [\text{Cu}^{2+}]$)? What should the slope of the line be equal to according to the Nernst equation? What is your value for the y-intercept? What is the significance of the y-intercept, that is, what does the y-intercept represent? What value should the y-intercept be?
PRELAB: Exp. 7  Galvanic Cells and the Nernst Equation

1. Using the following Standard Reduction Potential Table:

<table>
<thead>
<tr>
<th>Half-cell</th>
<th>$E^\circ$ (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^{+1}$ + 1 e$^{-1}$ $\rightarrow$ Ag(s)</td>
<td>+0.80 V</td>
</tr>
<tr>
<td>Cr$^{+3}$ + 3 e$^{-1}$ $\rightarrow$ Cr(s)</td>
<td>-0.74 V</td>
</tr>
</tbody>
</table>

Consider a galvanic cell consisting of the Ag$^{+1}$ (1.0 M) | Ag and the Cr$^{+3}$ (1.0 M) | Cr half-cells.

a) Which half-cell undergoes reduction?

b) Write an equation for the reaction that occurs at the anode and the reaction that occurs at the cathode.

c) What is the cell potential, $E^\circ_{\text{cell}}$, for this galvanic cell?

2. Use the Nernst equation to determine the cell potential, $E^\circ_{\text{cell}}$, of the galvanic cell consisting of the following two half-cells:

$$\text{Ag}^{+1} (0.0010 \text{ M}) + 1 \text{ e}^{-1} \rightarrow \text{Ag(s)} \quad \text{Cr}^{+3} (0.10 \text{ M}) + 3 \text{ e}^{-1} \rightarrow \text{Cr(s)}$$