An Electrochemistry Experiment

Name__________________________________________  Section_______________________

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ELECTROCHEMISTRY

LEARNING GOALS

1. Become familiar with redox reactions
2. Become familiar with half reactions
3. Become familiar with standard half cell potentials
4. Become familiar with the Nernst Equation

INTRODUCTION

Redox Reactions

Electrochemistry is the study of reactions that involve the transfer of electrons from one reactant to another to form new products. The reactant that gives up its electron(s) is called the reductant (or the reducing agent) and the reactant that accepts the electron(s) is called the oxidant (or oxidizing agent). The reductant is the species that undergoes oxidation, which is the loss of electrons. The oxidant is the species that undergoes reduction, which is the gain of electrons.

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

In the example above \(\text{Cu}^{2+}\) is the oxidant because it is gaining 2 electrons to form \(\text{Cu(s)}\) and \(\text{Zn(s)}\) is the reductant because it is losing two electrons to form \(\text{Zn}^{2+}\). Electrochemical reaction can always be split into two half reactions; one for the reduction and one for the oxidation. For this example,

Reduction half reaction \(\text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu(s)}\)

Oxidation half reaction \(\text{Zn(s)} \leftrightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^-\)

Notice if you add together the two half reactions the electrons cancel and it leaves you with the overall redox reaction. The electrons always have to balance this way because every mole of electrons being produced in the oxidation must be consumed in the reduction.

Electrochemical Cells

Batteries are devices that physically separate the reactants of a redox reaction in such a way that forces the exchange of electrons to flow through an external wire. This way the energy released from a favorable redox reaction can be harnessed and used to do work. The energy available for work increases with the equilibrium constant related of the redox reaction.
This is an electrochemical cell constructed for our redox reaction between \( \text{Cu}^{2+} \) and \( \text{Zn(s)} \). Notice the anode (where oxidation occurs) and the cathode (where reduction occurs) are compartmentalized so that the \( \text{Cu}^{2+} \) can not react directly on the surface of the zinc electrode. This way the electrons must flow from the anode to the cathode through the external wire. The salt bridge is necessary to prevent a build up of negative charge in the cathode compartment which would present a large energy barrier for the reaction to occur.

**Nernst Equation**

Theoretically, the cell potential, the potential difference across the two electrodes (anode and cathode), can be predicted by the Nernst Equation.

\[
E = (E_0^+ - E_0^-) - 0.05916/n \log Q
\]

\( E \) is the cell potential (EMF). \( Q \) is the reaction quotient of the overall redox reaction and \( E_0^+ \) and \( E_0^- \) are the standard reduction potentials for the reduction and oxidation half-cell reactions, respectively. The standard reduction potential of any half-reaction is arbitrarily defined relative to the half reaction for the oxidation of hydrogen gas. It represents the EMF for an electrochemical cell constructed such that the reduction half reaction is paired with the oxidation of hydrogen gas to \( \text{H}^+ (\text{aq}) \), at 298 K with all reactants and products at unit concentrations (1 M and 1 atm). Defining the standard reduction potentials of half-reactions is convenient because it enables us to construct a table of standard reduction potentials for a limited number of half-reactions that can than be used to determine the standard cell potentials \( (E_0^+ - E_0^-) \) for a much larger array of complete redox reactions. The equilibrium constant and \( (E_0^+ - E_0^-) \) is related through

\[
(E_0^+ - E_0^-) = 0.05916/n \log K
\]
Therefore, the larger the difference between the standard reduction potentials for the reduction and oxidation half-cell reactions, the larger the equilibrium constant.

Getting back to our cell, the standard reduction potential for the \( \text{Cu}^{2+}/\text{Cu(s)} \) half-cell is 0.337 V and the standard reduction potential for the \( \text{Zn}^{2+}/\text{Zn(s)} \) half-cell is -0.763 V. The Nernst Equation for cell shown above is

\[
E = (E^0_{\text{Cu}^{2+}/\text{Cu(s)}} - E^0_{\text{Zn}^{2+}/\text{Zn(s)}}) - 0.05916/2 \log \left( \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)
\]

\[
= \{0.337 – (-0.763)\} - 0.05916 \log (0.100/0.100)
\]

\[
= 1.096 \text{ V}
\]

One would expect the voltage measured across the electrodes of this cell to read about 1.1 V. Now, some energy is required to support the flow of electrons through the wire (ie. resistance), so often times the measured voltage is a bit less.

In the first part of this experiment you will construct miniature cells using a 24-well microplate to measure the cell voltages constructed with various metal ion/metal \( (\text{M}^{n+/\text{M(s)}}) \) pairs. Because the concentrations of all of the salt solution will be at 0.100 M, the cell potentials will be a measure of standard potential for the redox reaction \( (E^0_+ - E^0_-) \). You will compile the data to construct your own small table of standard reduction potentials.

**Concentration cells**

One can construct an electrochemical cell that utilizes the same half-cell reactions at both the anode and cathode. In this type of cell, the cell voltage is just a function of the ratio of the concentrations of the metal ion in anode and cathode. Here is an example.

\[
\text{Cu(s)} \bigg| \text{Cu}^{2+}(aq), 0.0100 \text{ M} \bigg\| \text{Cu}^{2+}(aq), 0.100 \text{ M} \bigg| \text{Cu(s)}
\]

Cathode \bigg\| \text{Anode}

(the double lines represent the salt bridge)

The Nernst Equation for cell shown below is

\[
E = (E^0_{\text{Cu}^{2+}/\text{Cu(s)}} - E^0_{\text{Cu}^{2+}/\text{Cu(s)}}) - 0.05916/2 \log \left( \frac{[\text{Cu}^{2+}]_{\text{Cathode}}}{[\text{Cu}^{2+}]_{\text{Anode}}} \right)
\]

\[
= \{0.337 – (0.337)\} - 0.05916/2 \log (0.0100/0.100)
\]

\[
= - 0.02958 \times (-1) = 0.02958 \text{ V} \text{ or about 29.6 mV}
\]

One would expect the voltage measured across the electrodes of this cell to read about 30 mV.
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If one knows the concentration of Cu²⁺ in the anode, one could use the Nernst Equation and the measured cell voltage to measure the concentration of an unknown copper solution used in the cathode compartment. For instance, if a 0.100 M solution is used in the anode compartment and a cell voltage of 85.1 mV is measured, the [Cu²⁺] of an unknown solution can be calculated by

\[
0.0851 = - \frac{0.05916}{2} \log\left(\frac{[\text{Cu}^{2+}]_{\text{unk}}}{0.100}\right)
\]

\[
0.0851 = \{- \frac{0.05916}{2} \log ([\text{Cu}^{2+}]_{\text{unk}})\} - \{-0.05916/2 \log (0.100)\}
\]

\[
0.0851 = -0.02958 \log [\text{Cu}^{2+}]_{\text{unk}} - 0.02958
\]

\[
\log [\text{Cu}^{2+}]_{\text{unk}} = (0.0851+0.02958)/(-0.02958)
\]

\[
[	ext{Cu}^{2+}]_{\text{unk}} = 10^{(0.0851+0.02958)/(-0.02958)} = 10^{(-3.88)} = 0.00013 \text{ M}
\]

In the second part of this experiment (Part B), you will construct a series of concentration cells using copper solutions of various concentrations and silver solutions of various concentrations. You will use the data to experimentally determine $\beta RT/F$ (or $\approx 0.059$).

In Part C you will also construct a concentration cell using a 0.100 M Cu(NO₃)₂ solution and an unknown solution, measure it cell potential and calculate the concentration of the unknown solution using the average value you obtained for $\beta RT/F$ in part B. (The $\beta$ is really just a fudge factor to account for a small loss in efficiency that usually occurs experimentally; it is often around 0.98).
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EXPERIMENTAL PROCEDURE

We will construct a series of miniature electrochemical cells using the wells of 24-well microplate plate. We will use KNO₃ soaked Kim-wipes as salt bridges, to allow charge neutralization between the wells.

![Diagram of 24-well plate]

PART A Building Your Own Activity Series

1) You have pieces of six metals, Zn, Cu, Mg, Ag, Pb and Fe, and 0.100 M solutions of each of their nitrate salts. Set up electrochemical cells with 0.100 M solution of the nitrate salts of each of the six metals in the 24-well plate. Each of the six solutions should be measure against the other five, for a total of 15 measurements. You should spend some preparation time mapping out which solution you plan on placing in which wells, strategically designing your template for efficiency to minimize waste.

2) Measure all possible combinations of metal ions that you have set up in the 24-well plate. When taking the measurements you will need to construct a salt-bridge by moistening a coiled Kim-wipe with 1.00 M KNO₃ solution, this will be done for every measurement you will take. You are using the pieces of metal as electrodes by dipping them in the appropriate solution in the cell. Remember: It is critical to match the metal with its own nitrate salt. A voltmeter will be used to make the measurements. Place the leads of the voltmeter on the metal electrodes that are dipped into the solution in the wells and read the voltage. Pay attention to which lead is on which metal. By convention, the $E^0$ of a Cu/Zn cell suggests that the Copper is acting as the cathode and therefore the positive lead should be placed on the Copper and the negative lead on the Zinc, for instance, giving a positive reading.
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PART B

For Part B of the experiment three of four groups should collaborate when diluting the 0.100M solution of copper and silver. This is done to minimize the waste.

1) Mix 10.0 mL of 0.100 M Cu(NO₃)₂ solution with 90.0 mL of 1.00 M KNO₃ in a 100 mL graduated cylinder to make 0.0100 M Cu(NO₃)₂ solution. Pour into a 200 mL beaker, label and save it. Further dilute the 0.0100 M Cu(NO₃)₂ solution by another factor of 10 by mixing 10.0 mL of it with 90.0 mL of 1.00 M KNO₃ solution in a 100 mL graduated cylinder to make 0.00100 M Cu(NO₃)₂ solution. Pour into a 200 mL beaker, label and save it. The volumes of these solutions are more than enough to be shared by four groups.

2) As done in part A of this experiment, set up three electrochemical cells with the three Cu(NO₃)₂ solutions and measure the voltage difference between all three. Remember to make salt-bridges for each measurement and to use Copper as the electrodes.

3) The same procedures, as outlined in 1) and 2), will be followed for the 0.100 M silver nitrate solution, again using Silver as the electrodes.

Part C

1) Determine the approximate concentration of the unknown Cu(NO₃)₂ solution by
   a. Constructing a concentration cell using the 0.100 M Cu(NO₃)₂ standard solution
   b. Measuring its cell potential
   c. Manipulating the Nernst Equation to solve for the concentration of Cu²⁺ in the unknown.

Report:

- Write an abstract (10 pts)
- Tabulate your data. (10 pts)
- Part A: Produce a table of E⁰ for the standard half cell reduction potentials for these six metals, similar to the one in Table 20.1 in your textbook. To do this assume the Ag⁺,Ag₉(s) is 0.80 V. Compare your values with the values given in Appendix E of your text. (15 pts)
- Part B: Discuss the agreement between your measurements of each of the concentration cells and theory, as predicted by the Nernst Equation. (15 pts)
- Part C: Report the voltage measured and the concentration of the unknown, as calculated from the measured voltage and your value for βRT/F in part B. (10 pts)