Experiment 21D

THE ELECTROCHEMICAL ACTIVITY SERIES AND BATTERIES

MATERIALS:
Four 50 mL beakers; 400 mL beaker; glass marking pen; stirring rod; large watch glass; plastic dropper; stainless steel spatula; double-pole double-throw (DPDT) switch; Hubble plug, light bulb and lamp socket; voltmeter/ohmmeter; four leads with clips; sandpaper; Zn plate; wood block; carbon block; filter paper and 1 cm x 13 cm filter paper strips; strips of metals (2 Pb, Cu, Zn); Ag wire; 3.6 M H₂SO₄; 0.25 M solutions of Cu(NO₃)₂, Zn(NO₃)₂ and AgNO₃; 1.5 M NaNO₃ solution; concentrated NH₃ solution (dropper bottle); MnO₂; plastic block.

PURPOSE:
The purpose of this experiment is to experimentally rank the electrochemical reactivity of several metals, and to construct the electrochemical cells that can be made from spontaneous reactions of those elements. Some commercial cells will also be examined.

LEARNING OBJECTIVES:
By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Write an electrochemical Activity Series based on experimental observations.
2. Predict the products of a redox equation using a table of reduction potentials.
3. Define the following terms: oxidation, reduction, oxidizing agent, reducing agent, electrochemical activity series, battery; primary battery; secondary battery; electrode; electrolyte; charging; discharging.
4. Explain the use and purpose of a salt bridge.
5. Identify an electrode as either a cathode or an anode.
6. Write the half reaction occurring at each electrode and a complete balanced overall reaction for an electrochemical cell.
7. Use the Nernst equation to calculate cell voltage.

DISCUSSION:
Elements, both metallic and nonmetallic, vary in their tendencies to undergo reactions. In the case of oxidation-reduction (redox) reactions, this reactivity is a measure of the ease with which the elements gain or lose electrons. Metals tend to lose electrons (be oxidized) to form cations, while nonmetals tend to form anions by gaining electrons (undergoing reduction). The relative reactivity of metals is a matter of practical importance in the civilian world and in the Navy, having an impact on construction materials, batteries, corrosion, etc. In this experiment, we will compare the behavior of several metals in oxidation processes, and use the data collected to create a list of metals in decreasing order of reactivity. This “activity series” can be used to predict reactions in many electrochemical processes. These same spontaneous redox reactions can be utilized as an electrochemical cell or battery by careful arrangement of the reacting species. We will construct and examine several such cells, and some well-known commercial batteries as well.

For metals that do not react with water, there is a simple way to determine the relative reactivities of the elements. This involves a “displacement reaction”, where one element displaces (pushes out) a second element from its compound. An example is the reaction between cadmium metal and gold(III) nitrate solution, written in both molecular and net ionic form:

\[
3 \text{Cd (s)} + 2 \text{Au(NO}_3\text{)}_3 \text{(aq)} \rightarrow 2 \text{Au (s)} + 3 \text{Cd(NO}_3\text{)}_2 \text{(aq)} \quad (1)
\]

\[
3 \text{Cd (s)} + 2 \text{Au}^{3+} \text{(aq)} \rightarrow 2 \text{Au (s)} + 3 \text{Cd}^{2+} \text{(aq)} \quad (2)
\]

It is clear that this is a redox reaction. Cadmium metal loses electrons (is oxidized) to form Cd²⁺, while gold(III) ions are reduced (gain electrons) to form metallic gold. The half-reactions are:
3 ( Cd (s) → Cd²⁺ (aq) + 2 e⁻ ) oxidation (3)

2 ( 3 e⁻ + Au³⁺ (aq) → Au (s) ) reduction (4)

\[
3 \text{ Cd (s)} + 2 \text{ Au}^{3+} (\text{aq}) \rightarrow 2 \text{ Au (s)} + 3 \text{ Cd}^{2+} (\text{aq})
\] overall (5)

Experimentally, it would be observed that the cadmium dissolves, while a layer of gold metal would plate out on the remaining cadmium. Experiments also indicate that the reverse reaction, between metallic gold and dissolved cadmium ions, does not occur:

\[
\text{Au (s) + Cd}^{2+} (\text{aq}) \rightarrow \text{no reaction}
\] (6)

Gold does not displace cadmium from cadmium nitrate. Therefore, cadmium must be a more active metal (more willing to lose electrons) than is gold.

In this example, since cadmium causes gold(III) ion to gain electrons, cadmium is called the reducing agent. (A reducing agent causes something else to be reduced and is itself oxidized.) The gold(III) ion is reduced to form the neutral metal atom, so Au⁺⁺ is the oxidizing agent. (An oxidizing agent causes something else to be oxidized and is itself reduced.) When such comparisons are made for many pairs, the result is an Activity Series. Written in terms of the oxidation step, the activity series would include:

<table>
<thead>
<tr>
<th>Best</th>
<th>Reduced form → Oxidized form + Electrons</th>
<th>Worst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K → K⁺ + 1 e⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn → Mn²⁺ + 2 e⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd → Cd²⁺ + 2 e⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb → Pb²⁺ + 2 e⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au → Au⁺⁺ + 3 e⁻</td>
<td></td>
</tr>
<tr>
<td>Worst</td>
<td>Oxidizing Agents</td>
<td>Best</td>
</tr>
</tbody>
</table>

Metals at the top left-side of the list (e.g., K) can be oxidized most easily; therefore, they are good reducing agents. The elements at the bottom of the list such as gold, Au, do not readily undergo oxidation, so they are poor reducing agents. However, the oxidized form (Au⁺⁺) will readily gain electrons (i.e. undergo reduction), so Au⁺⁺ is a relatively good oxidizing agent. The utility of the activity series results from the fact that any metal on the list is able to displace the elements below it from their compounds by a spontaneous redox reaction. A more general statement of the same behavior is that the reduced form of an element on the activity list will react spontaneously with the oxidized form of any element lower on the list. Nonmetals can be added to the list by conducting redox reactions similar to those discussed for metals. Incorporating those results into the table expands the utility of the table as a prediction tool.

The observation of spontaneous reactions between a metal and the dissolved ion of a second metal was used above as the basis of ranking the relative reactivities of the two metals. If the two reactants were placed in contact, and a reaction occurred spontaneously, there must have been a driving force available. Stated another way, G for the reaction must have been negative; that also means that there was energy available to do work. An electrochemical cell is a device constructed in such a way that the work of a spontaneous redox reaction can be made available as electrical energy. The key to doing so is to NOT permit direct contact between the reactants, but to allow only indirect contact. The more active element still undergoes oxidation, losing electrons to the less active species. However, in a cell, these electrons are shunted through an external wire. Since that external wire can be connected to a light bulb, motor, etc., useful electrical work can be obtained.

Consider the reaction between cadmium metal and gold(III) ions discussed above. The same reaction can be set up in two different ways, as shown in Figure 1. The first allows direct contact of the reactants, and does not provide useful electrical work. The second involves only indirect contact of the reactants; this device is an electrochemical cell. Electrons still move from the Cd metal to the Au³⁺ ions, but do so through the external circuit.
Figure 1. Spontaneous Electrochemical Reactions

The two metal rods in the cell are called electrodes. The anode is the electrode where oxidation occurs; here, it is the Cd metal. Reduction takes place at the Au electrode; it is the cathode. The signs of the electrodes are defined by the direction of electron flow in the external circuit. Since the negative electrons are moving towards the gold cathode, it must be positive. Similarly, the cadmium anode, as the source of the electrons, must be negative. This convention (+ for cathode and – for anode) is true for all spontaneous electrochemical cells (but is opposite that of the nonspontaneous electrolytic cells). The other new feature in the cell figure above is the inverted U-tube, called a salt bridge, connecting the two beakers (half-cells). The salt bridge is necessary to complete the electrical circuit. No electrons flow through the salt bridge, but instead ions carry charge between the two half-cells. Looking at reactions (3) and (4), it is clear that the cathode compartment becomes increasingly more negatively charged, as Au$^{3+}$ ions are consumed, and the anode half-cell becomes more positively charged, as Cd$^{2+}$ is formed. Without the salt bridge, the reaction would rapidly end because of this charge imbalance. The salt bridge, which contains non-reactive ions, allows the charges to equalize and maintain overall cell electroneutrality.

A battery is an electrochemical cell or group of cells that uses a chemical reaction to produce electricity. These devices are available in a wide variety of designs and are especially useful when mobility or high efficiency is of primary importance. Batteries that are not rechargeable are classified as primary batteries. Examples include the dry cell (Zn-MnO$_2$ cell) and the alkaline-manganese cell, both of which are often used in flashlights and battery-powered toys. The alkaline-manganese cell provides a steadier voltage under heavy current drain than the dry cell. Its higher cost, relative to a standard dry cell, is due to the more elaborate construction required to prevent leakage of the concentrated NaOH electrolyte solution. Both the dry cell and the alkaline-manganese cells are sealed systems. Because of this, no attempt should ever be made to recharge these batteries; there is a high possibility of explosion due to the formation of a gas inside the sealed container during recharging.

Batteries that can be recharged are known as secondary batteries. These include the lead storage battery used in automobiles and the nickel-cadmium (nicad) battery used in hand calculators, rechargeable flashlights, cordless electric shavers and hand tools. A completely sealed nickel-cadmium battery is much more stable than a lead storage battery and, unlike the lead storage battery whose voltage decreases on discharge, the nicad battery provides a fairly constant voltage on discharge. The main drawback of nicad batteries is their “charge memory” problem. Upon repeated shallow discharging (and recharging), the battery remembers that discharge voltage and fails to discharge past that point again. This was a serious problem with wireless and cellular phones batteries, and these systems now use nickel metal hydride and lithium batteries as the primary sources of power instead.

In this experiment, the construction of lead storage batteries and dry cells will be explored. Of particular interest are the oxidation-reduction reactions that occur in each of these two types of batteries.

I. The Lead Storage Battery

A 12 volt lead storage battery (Figure 2), such as those found in automobiles, consists of six cells arranged in series. Each cell in a lead storage battery develops about 1.9 volts when fully charged and is composed of two electrodes of lead alloy grids immersed in a solution of sulfuric acid. One electrode is packed with a spongy lead to form the anode, where oxidation occurs. The other electrode is packed with lead(IV) oxide and forms the cathode, where
During discharge, when current is being drawn from the cell, the half-cell reactions are:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>$\text{Pb (s) + SO}_4^{2-} \text{(aq)} \rightarrow \text{PbSO}_4 (s) + 2 e^-$ (7)</td>
</tr>
<tr>
<td>Cathode</td>
<td>$\text{PbO}_2 (s) + 4 \text{H}^+ (aq) + \text{SO}_4^{2-} (aq) + 2 e^- \rightarrow \text{PbSO}_4 (s) + 2 \text{H}_2\text{O (l)}$ (8)</td>
</tr>
</tbody>
</table>

The reverse reactions take place when the battery is recharging and the anode and the cathode are reversed. The equation for the overall cell reaction is obtained by adding together the equations for the two half-reactions:

$$\text{discharge} \quad \text{Pb (s) + PbO}_2 (s) + 2 \text{H}_2\text{SO}_4 (aq) \rightleftharpoons 2 \text{PbSO}_4 (s) + 2 \text{H}_2\text{O (l)} \quad (9)$$

As sulfuric acid is consumed and water is produced during the discharge process, the concentration of the sulfuric acid decreases. This leads to a decrease in the cell voltage output of the battery as the battery electrolyte solution is diluted.

The lead storage battery constructed in this experiment must be charged before its initial use to produce the lead(IV) oxide required. During the initial charging, the reactions taking place at the anode are:

$$\text{Pb (s) + 2 H}_2\text{O (l)} \rightarrow \text{PbO}_2 (s) + 4 \text{H}^+ (aq) + 4 e^- \quad (10)$$

and

$$2 \text{H}_2\text{O (l)} \rightarrow 4 \text{H}^+ (aq) + \text{O}_2 (g) + 4 e^- \quad (11)$$

At the cathode, the reaction during charging is:

$$2 \text{H}^+ (aq) + 2 e^- \rightarrow \text{H}_2 (g) \quad (12)$$

If a lead storage battery is overcharged, large amounts of $\text{H}_2 (g)$ and $\text{O}_2 (g)$ may be formed by the above reactions at the electrodes indicated. There is always a possibility of explosion if the hydrogen gas undergoes a combustion reaction as shown in equation (13). For this reason, flames or sources of sparks should never be brought near a lead storage battery while it is being charged.

$$2 \text{H}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O (g)} \quad (13)$$
II. The Dry Cell

The dry cell is a primary cell that cannot be recharged. It must be discarded after it has been completely discharged. This cell (see Figure 3) has a zinc cylinder (called a can) as the anode and a carbon rod as the cathode. The can is filled with a paste containing the electrolyte, ammonium chloride, and the depolarizer, manganese(IV) oxide. The can itself is lined with a porous paper (called the separator) in order to keep the manganese(IV) oxide from coming into contact with the zinc walls of the can. With no manganese(IV) oxide present, the electrode reactions would be:

\[
\text{anode: } \text{Zn (s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2 \text{ e}^- \quad (14)
\]

\[
\text{cathode: } 2 \text{ NH}_4^+ (\text{aq}) + 2 \text{ e}^- \rightarrow 2 \text{ NH}_3 (\text{aq}) + \text{H}_2 (\text{g}) \quad (15)
\]

If this cathode reaction were permitted to take place to any appreciable extent, the hydrogen, H₂, produced would soon coat the cathode, insulating it from the rest of the cell and resulting in a phenomenon called polarization. No current would flow. However, with manganese(IV) oxide present, no hydrogen is produced. Instead, the manganese(IV) oxide is reduced to manganese(III) hydroxide, Mn(OH)₃, and the cathode reaction then becomes:

\[
2 \text{ MnO}_2 (\text{s}) + 2 \text{ NH}_4^+ (\text{aq}) + 2 \text{ H}_2\text{O (l)} + 2\text{e}^- \rightarrow 2 \text{ Mn(OH)}_3 (\text{s}) + 2 \text{ NH}_3 (\text{aq}) \quad (16)
\]

The complete electrochemical reaction for the cell is given by the following equation.

\[
\text{Zn (s)} + 2 \text{ MnO}_2 (\text{s}) + 2 \text{ NH}_4^+ (\text{aq}) + 2 \text{ H}_2\text{O (l)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2 \text{ Mn(OH)}_3 (\text{s}) + 2 \text{ NH}_3 (\text{aq}) \quad (17)
\]

The released NH₃ forms a complex ion with Zn²⁺, as shown below.

\[
\text{Zn}^{2+} (\text{aq}) + 4 \text{ NH}_3 (\text{aq}) \rightarrow \text{Zn(NH}_3)_4^{2+} (\text{aq}) \quad (18)
\]

Figure 3. Dry Cell Battery
PROCEDURE:

Part A. Reactions of Metals with Metal Ions

1. Place about 10 mL of 0.25 M AgNO₃ solution in one 50 mL beaker; 10 mL of 0.25 M Cu(NO₃)₂ solution in a second 50 mL beaker; and 10 mL of 0.25 M Zn(NO₃)₂ solution in a third 50 mL beaker. (Be careful with the AgNO₃; it can stain your skin!) Label the beakers.

2. Identify the silver wire and strips of copper and zinc metals. Clean the metal surfaces with sandpaper, if necessary. Place each metal, one at a time, in the solutions of the other two metal ions (i.e., there is no need to test Cu metal in Cu(NO₃)₂ solution). Allow them to stand in the liquid for about 30 seconds each. Watch carefully for evidence of any reaction, such as the dissolution or darkening of the metal, continuous evolution of a gas, or the appearance of a new color in the liquid. (If an obvious reaction begins rapidly, observe briefly and then remove the sample.) Remove each strip before testing the next metal; examine it carefully outside the bath, as color changes of the solid may not be apparent while the samples are still in a colored liquid. Be sure to rinse off the strips with water after immersion in any bath; clean the surface with sandpaper if the metal became discolored in a previous bath. Record your observations in the appropriate table in the DATA SECTION. Save your solutions for Part B.

Part B. Construction of Electrochemical Cells (Batteries)

1. In the DATA SECTION, list the combinations of metal plus metal ion solution that led to a spontaneous reaction in Part A. These are the combinations that can be used to create electrochemical cells. Have your instructor check your list before proceeding.

2. Use the metal strips and small beakers of metal ion solutions to construct an electrochemical cell from your first combination as described below. First, place the two beakers next to each other in the plastic block provided. Next, clean the metal strip with sandpaper, rinse it with distilled water, and place it in a solution containing ITSELF ion (e.g., place the Cu strip in the Cu²⁺ solution, etc.). Next, take the metal ion solution, and place in it a cleaned strip of the same metal (e.g., in the Ag⁺ solution, place the Ag wire). These beakers, with their metal electrodes, will constitute the ‘half-cells’ of your batteries.

3. Make sure the metal strips are not in contact. Take your voltmeter and attach the leads to the two electrodes. It is VERY important that you have good contact; it may be useful to sand the metal at the contact point. Set the voltmeter on the 2000m DC V scale. There should be no voltage, as the circuit is incomplete. What’s missing?

4. Close the circuit with a ‘salt bridge’ between the two beakers. For the salt bridge, use a strip of filter paper that has been soaked in 1.5 M NaNO₃ solution. The strip should extend from the liquid in the first beaker, over the edges where the beakers are in contact, and end in the liquid of the second beaker. Each end MUST be below the liquid level. Make sure the salt bridge doesn’t touch the metal electrodes. Record the positive voltage, with the proper units, in the DATA SECTION. (If the voltage is negative, just reverse the leads.) Identify the negative electrode; this is the metal connected to the voltmeter ‘COM’ terminal, when the voltage reads a positive value.

5. Repeat steps 2-4 with each of the other combinations that gave a spontaneous reaction in Part A. Use a fresh salt bridge strip for each cell.

Part C. Further Examinations of a Cell

1. Reconstruct the cell involving the Cu in Cu²⁺ and Zn in Zn²⁺ solutions, using fresh solutions (10 mL each) and a new salt bridge strip. Measure and record the cell voltage.

2. How important are each of the components for operation of the cell? Find out as follows. Remove the Cu strip, and replace it with a spatula, which serves as an “inert” conductor. Record the voltage.

3. Restore the Cu strip, and remove the Zn strip, replacing it with the spatula. Record the voltage.

4. Remove the spatula and restore the Zn strip, returning the cell to its original arrangement. Replace the salt bridge with a fresh one. Record the voltage to be sure it is close to the original value.

5. Change the concentration of the Zn²⁺ by adding ~1 g of solid Zn(NO₃)₂ (an unpacked 1 g sample is about the size of a sugar cube) to the beaker containing Zn²⁺. Stir the solution, and record the voltage. Make sure the salt bridge doesn’t touch the electrodes.

6. Remove the salt bridge strip, and discard the last Zn²⁺ solution. Replace it with ~10 mL of fresh 0.25 M Zn(NO₃)₂ solution. Replace the salt bridge with a fresh strip. Now change the concentration of Cu²⁺ by adding 20 drops of concentrated NH₃ solution to the Cu²⁺/Cu half-cell. Stir the solution, and record your observations and voltage.

Part D. Commercial Cells – The Lead Storage Battery
1. In the hood, clean the two lead strips with sandpaper. Make sure the lead shavings go into the proper waste container and do not inhale the lead dust.
2. Hang the lead strips on opposite sides of a 400 mL beaker containing approximately 300 mL of 3.6 M sulfuric acid. Make sure that the strips do not touch each other.
3. Connect the flashlight bulb, voltmeter, battery, and DPDT switch as shown in Figure 4, but leave one wire to the light bulb disconnected so that the light bulb is not, for now, in either circuit.

Figure 4. Lead Battery Circuit

Have your instructor check all connections before proceeding.  

   _____________________
   Instructor's initials

4. After the instructor has certified that the connections are correct, plug the circuit into the designated DC power source. Close the switch by moving the lever to the right and begin charging the battery.
5. After the battery has been charging for about five minutes, throw the switch to the voltmeter side. Record the voltage of the cell in the DATA SECTION. (If the voltmeter indicates a negative value, reverse the leads to the voltmeter.)
6. Now connect the light bulb wire, placing the light bulb into the battery/voltmeter circuit. Note that the voltage on discharge drops quite slowly. When the cell is almost completely discharged, the voltage suddenly drops very rapidly. This is a characteristic of the lead storage cell.
7. Charge the battery again for a few minutes. Open the switch and examine the electrodes. Note the formation of lead(IV) oxide on one electrode and record its color in the DATA SECTION.
8. Upon completion of this part of the experiment, unplug the circuit from the power source. Disassemble the switch and all of the electrical wiring. Do NOT dispose of the H2SO4 solution since it can be reused by another class.

Part D. Commercial Cells – The Dry Cell

CAUTION: Before beginning this procedure, be sure the DPDT switch is not connected to the power source.

1. Connect the carbon block, using a battery clip on one corner, and the zinc plate to the central terminals of the DPDT switch. Then connect the voltmeter leads to these same terminals.
2. The instructor will prepare a paste consisting of MnO2 and saturated aqueous NH4Cl.
3. Place the zinc plate on the wooden square. See Figure 5.

Figure 5. Dry Cell

4. Wet a piece of filter paper with saturated aqueous NH4Cl solution, place it on the zinc plate and tear off the overhanging edges. Obtain enough of the MnO2 paste from your instructor to completely cover the paper.
5. With the switch to the light bulb open, place the carbon block on the paste and press down on it firmly. The block assembly should be as shown in Figure 5. Record the voltage of the cell in the DATA SECTION.
6. Close the switch to the light bulb. Observe any changes in the voltage reading. Reopen the switch to the light bulb and continue to make observations of the voltage reading. Describe the fluctuations in voltage upon connecting and disconnecting the light bulb in the DATA SECTION. Be clear and complete.
7. Upon completion of this part of the experiment, disassemble the apparatus. Place the filter paper coated with the MnO\textsubscript{2} paste in the trash. Clean the carbon block and the zinc plate by rinsing them with water in the sink.

**Clean-up:**

1. Disassemble your circuits, turn off the voltmeter, and leave the equipment where it was originally found.
2. Discard used salt bridge filter strips in the trash.
3. Do NOT discard the H\textsubscript{2}SO\textsubscript{4} solution used for the lead-acid battery. This may be reused by another class.
4. Rinse all glassware and return them to their proper original locations.
5. Wash your hands before leaving lab.
Part A. Reactions of Metals with Metal Ions

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal Ion</th>
<th>Rxn? (Y/N)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>Ag &lt;sup&gt;+&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Ag &lt;sup&gt;+&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Part B. Construction of Electrochemical Cells (Batteries)

Combinations of metal plus metal ion solution that gave spontaneous reactions:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal Ion Solution</th>
<th>Voltage</th>
<th>Negative Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Instructor’s Initials _______________________

Part C. Further Examinations of a Cell

Original cell voltage of Cu-Zn cell

Voltage of cell when Cu strip is replaced by spatula

Voltage of cell when Zn strip is replaced by spatula

Voltage of cell when restored to its original configuration

Voltage of cell when solid Zn(NO<sub>3</sub>)<sub>2</sub> is added

Voltage of cell when concentrated NH<sub>3</sub> solution is added

Observations: ________________________________________________________________

Part D. Commercial Cells – The Lead Storage Battery
Cell voltage of the lead storage battery

Color of the PbO₂(s) formed

Commercial Cells – The Dry Cell

Original cell voltage of the dry cell

Observations about the dry cell voltage:

________________________________________________________________________________________

________________________________________________________________________________________

________________________________________________________________________________________

________________________________________________________________________________________
DATA TREATMENT  
Experiment 21D

Part A. Reactions of Metals with Metal Ions

(A.1) Write oxidation half-reactions for the metals Ag, Cu, and Zn. Use the format found in the table on page E21D-2.

Ag:

Cu:

Zn:

(A.2) Consider the elements Ag and Cu. Knowing that the reduced form of one element will react spontaneously with the oxidized form of an element lower on the activity series list, use your observations of the reactions in Part A to determine which of the two is higher and which is lower in the series. Explain your reasoning.

Higher: ______________   Lower: ______________

(A.3) Using the same logic, add Zn to your list, and write the activity series featuring the three metals (Ag, Cu, Zn), listed from most active to least active.

most active __________

________

least active __________

(A.4) Use the following information to properly locate your three elements (Ag, Cu, Zn) into the activity series on page E21D-2. Write out the series featuring all eight metals.

<table>
<thead>
<tr>
<th>Activity Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn reacts with Cu^{2+}, Ag^{+}, and Zn^{2+}</td>
</tr>
<tr>
<td>Zn reacts with Cd^{2+}</td>
</tr>
<tr>
<td>Cd and Pb both react with Cu^{2+}</td>
</tr>
<tr>
<td>Au does NOT react with Cu^{2+}, Ag^{+}, or Zn^{2+}</td>
</tr>
</tbody>
</table>

most active __________

________

________

________

________

least active __________

Part B. Construction of Electrochemical Cells

E21D-11
(B.1) For the three cells you constructed in Part B, identify the anode and cathode materials. Construct your list in order of DECREASING cell voltage. The sign of the electrode (or its connection to the voltmeter) could help you decide which was the anode.

<table>
<thead>
<tr>
<th>Measured Voltage</th>
<th>Anode Metal</th>
<th>Cathode Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>(highest)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(lowest)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(B.2) Consider the identities of each metal pair listed in (B.1), and relate their relative positions to the Activity Series just generated (in (A.3)). Do they agree? Explain.

(B.3) The measured voltages essentially represent a difference in potential energy between the two metals in each cell. Does that pattern agree with the Activity Series? Explain.

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Part C. Further Examinations of a Cell

(C.1) Write the overall cell reaction for the cell constructed in Part C of the experiment. Remember that this was a spontaneous reaction giving a positive potential.

(C.2) Based on your data, which specific metal, copper or zinc, was found to be essential for the operation of the cell in Part C? Using the overall cell reaction, explain why this is the case.

(C.3) Explain why the cell voltages increased or decreased when the solution concentrations (of Cu^{2+} and Zn^{2+}) were changed. Use the Nernst equation to support your explanation.
(C.4) Calculate the theoretical voltage that can be obtained from a Cu-Zn cell under standard conditions. Show your work. Obtain Standard Reduction Potentials (E° values) for half reactions from the appropriate Appendix of your textbook.

(C.5) How does the result of (C.4) compare to the cell voltage you measured? Suggest reasons for any discrepancy.

Part D. Commercial Cells - The Lead Storage Battery

(D.1) When seawater, which can be considered to be NaCl (aq), is allowed to enter a lead storage battery, Cl⁻ (aq) is oxidized by the PbO₂ (s) to generate Cl₂ (g). The presence of toxic chlorine gas in a confined space, such as on a submarine, is unpleasant at low concentrations and fatal at higher concentrations. For this reason, elaborate precautions are taken to exclude seawater from the battery compartment of a submarine. In addition to Cl₂ (g), PbCl₂ (s) is also formed.

Using the half-reaction method, write a complete, balanced net ionic equation for this reaction process. Identify the reactants and products and remember that the reaction is occurring in an acidic, aqueous solution.

Commercial Cells - The Dry Cell
(D.2) Use equation (17) and the Nernst Equation to aid in answering the following questions.

a. Explain how the voltage of a dry cell battery would be affected by a buildup or increase of Zn$^{2+}$ ions near the anode.

b. If, over time, the Zn$^{2+}$ ions migrate away from the anode or are consumed by reaction with the NH$_3$ (see equation (18)), what effect would this have on the recorded voltage? Explain your answer.

(D.3) In an alkaline flashlight battery, the reactants are Zn (s) and MnO$_2$ (s), but the electrolyte solution is NaOH (aq) instead of the acidic NH$_4$Cl (aq). Under these basic conditions, the products are ZnO (s) and Mn$_2$O$_3$ (s). For this battery, write and balance the overall equation.