Experiment 21B

FV - 30 March 2000

THE CHEMISTRY OF CELLS AND STORAGE BATTERIES

MATERIALS: Three 400 mL beakers, 10 mL graduated cylinder, 100 mL graduated cylinder, stirring rod, evaporating dish, U-tube, double-pole double-throw (DPDT) switch, light bulb and lamp socket, voltmeter/ohmmeter, four leads, sandpaper, strips of metals (Pb, Cu, Al, Zn), Zn plate, wood block, carbon block, filter paper, scoopula, MnO_2, 3.6 M H_2SO_4, saturated NH_4Cl solution, 1 M $CuSO_4$, 1 M KNO_3, 6 M NaOH.

PURPOSE: The purpose of this experiment is to construct both a primary battery and a secondary battery and to observe their properties.

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

1. Define the terms: battery; primary battery; secondary battery; electrode; electrolyte; charging; discharging.
2. Explain the use and purpose of a salt bridge.
3. Identify an electrode as either a cathode or an anode.
4. Write the half reaction occurring at each electrode and a complete balanced overall reaction for an electrochemical cell.
5. Use the Nernst equation to calculate cell voltage.

DISCUSSION:

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. In addition, batteries can be adapted to address a wide range of applications and power requirements. Some batteries, such as car batteries, produce very high currents for short time periods. Others provide stable voltages under low current drain over a long period of time, *e.g.* a heart pacemaker battery.

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 cell 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.

A. The Lead Storage Battery

A 12 V lead storage battery (Figure 1), 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 the reduction half-reaction takes place. During discharge, when current is being drawn from the cell, the half-cell reactions are:

anode: $$Pb\,(s) + SO_4^{2-}\,(aq) \rightarrow PbSO_4\,(s) + 2\,e^- \qquad (1)$$

cathode: $$PbO_2\,(s) + 4\,H^+\,(aq) + SO_4^{2-}\,(aq) + 2\,e^- \rightarrow PbSO_4\,(s) + 2\,H_2O\,(l) \qquad (2)$$

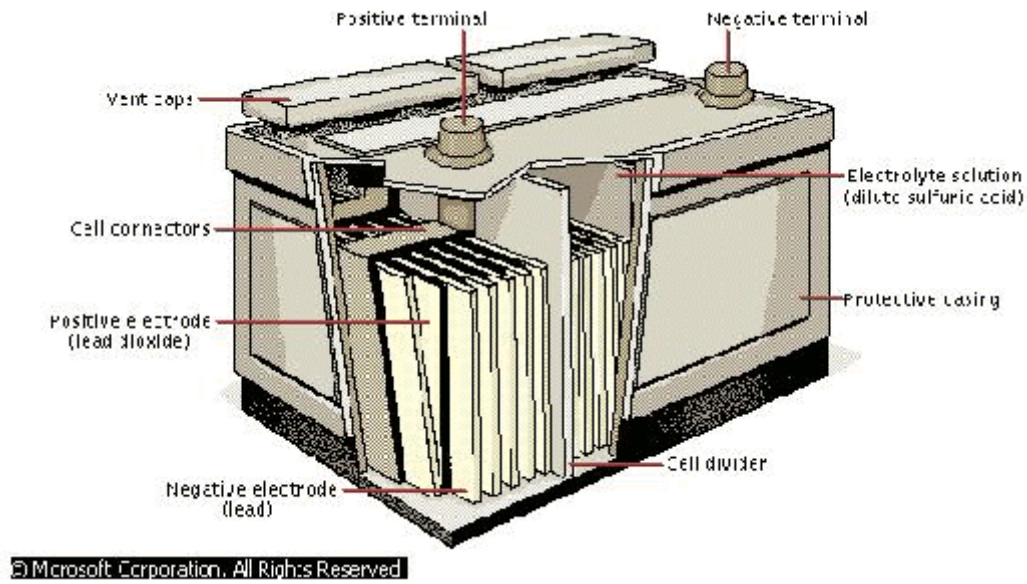


Figure 1. The Lead Storage Battery

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:

$$Pb\,(s) + PbO_2\,(s) + 2\,H_2SO_4\,(aq) \underset{\text{recharge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2\,PbSO_4\,(s) + 2\,H_2O\,(l) \qquad (3)$$

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:

$$Pb\ (s) + 2\ H_2O\ (l) \rightarrow PbO_2\ (s) + 4\ H^+\ (aq) + 4\ e^- \qquad (4)$$

and

$$2\ H_2O\ (l) \rightarrow 4\ H^+\ (aq) + O_2\ (g) + 4\ e^- \qquad (5)$$

At the cathode, the reaction during charging is:

$$2\ H^+\ (aq) + 2\ e^- \rightarrow H_2\ (g) \qquad (6)$$

If a lead storage battery is overcharged, large amounts of $H_2(g)$ and $O_2(g)$ 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 (7). For this reason, flames or sources of sparks should never be brought near a lead storage battery while it is being charged.

$$2\ H_2\ (g) + O_2\ (g) \xrightarrow{\text{spark}} 2\ H_2O\ (g) \qquad (7)$$

B. 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 2) 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:

anode: $$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2\ e^- \qquad (8)$$

cathode: $$2\ NH_4^+\ (aq) + 2\ e^- \rightarrow 2\ NH_3\ (aq) + H_2\ (g) \qquad (9)$$

If this cathode reaction were permitted to take place to any appreciable extent, the hydrogen, H_2, 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:

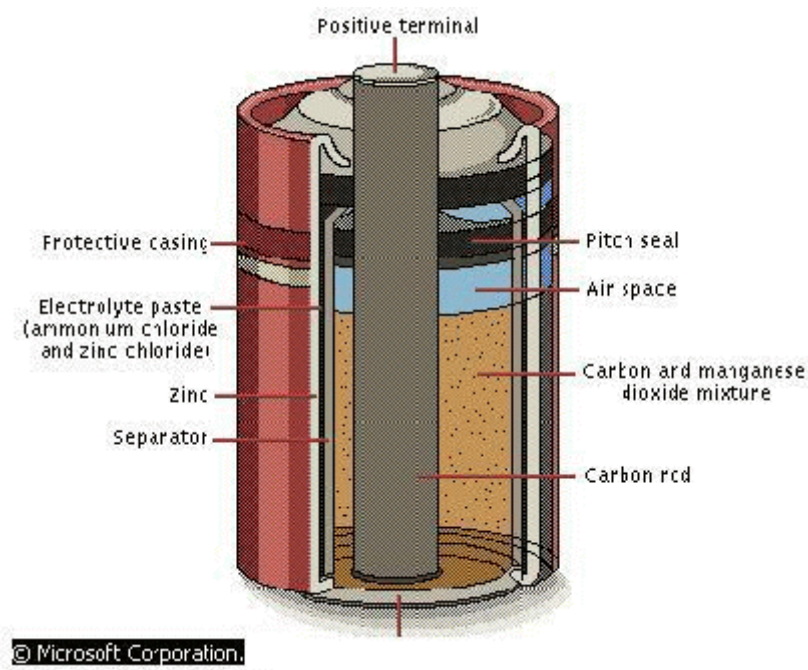
$$2\ MnO_2\ (s) + 2\ NH_4^+\ (aq) + 2\ H_2O\ (l) + 2e^- \rightarrow 2\ Mn(OH)_3\ (s) + 2\ NH_3\ (aq) \qquad (10)$$

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

$$Zn\ (s) + 2\ MnO_2\ (s) + 2\ NH_4^+\ (aq) + 2\ H_2O\ (l) \rightarrow Zn^{2+}\ (aq) + 2\ Mn(OH)_3\ (s) + 2\ NH_3\ (aq) \qquad (11)$$

The released NH_3 forms a complex ion with Zn^{2+}, as shown below.

$$Zn^{2+}\ (aq) + 4\ NH_3\ (aq) \rightarrow Zn(NH_3)_4^{2+}\ (aq) \qquad (12)$$



Negative Terminal

Figure 2. Dry Cell Battery

C. Other Electrochemical Cells

A galvanic cell is an electrochemical cell in which the oxidation and reduction reactions occur spontaneously. For a galvanic cell to produce useful electrical current, the two half-reactions must be physically separated from each other. In the apparatus used in this experiment (Figure 3) the reactions take place in separate beakers. The beaker in which reduction will take place contains a copper(II) sulfate solution and a strip of copper metal. The oxidation will take place in a beaker containing a metal strip and a potassium nitrate solution. The potassium nitrate serves as an electrolyte and is not directly involved in the reaction. No reaction will take place until these beakers are connected to form a complete circuit. One part of the connection is supplied by the wire, with a switch and voltmeter, connecting the metal strips. The electrons follow this path and their motion represents the current used to power a motor, or light bulb. A salt bridge provides the other connection. This completes the circuit by allowing the flow of charged particles through the solution.

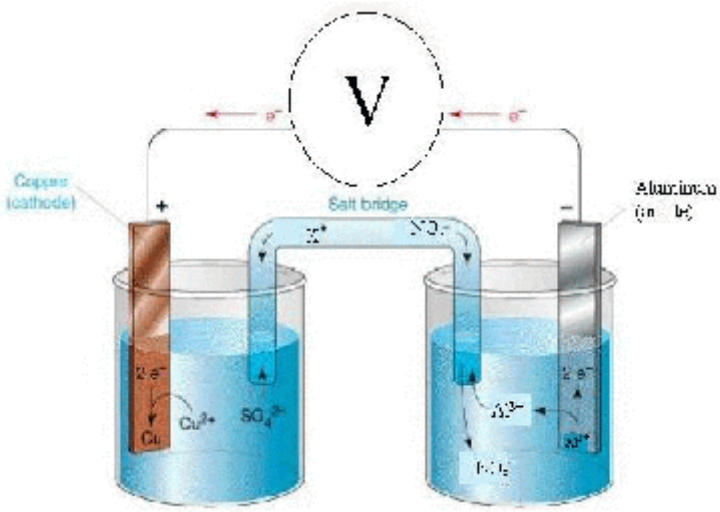


Figure 3. Galvanic Cell

PROCEDURE:

Part A. The Lead Storage Battery

1. In the hood, clean the two lead strips with sandpaper and hang them 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.

2. 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.

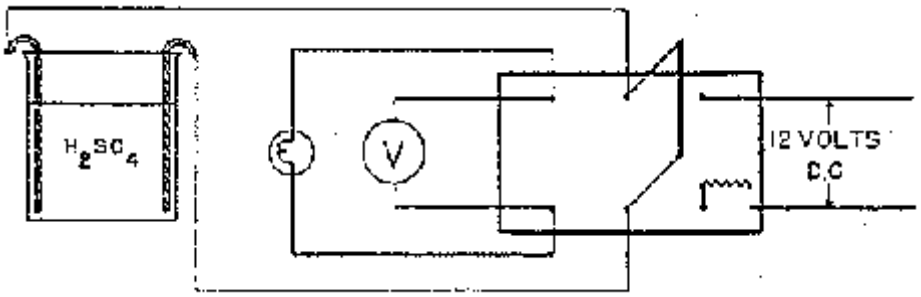


Figure 4. Lead Battery Circuit

Have your instructor check all connections before proceeding. _____

Instructor's initials

3. 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.

4. 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.)

5. 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.

6. 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.

7. Upon completion of this part of the experiment, disassemble the switch and all of the electrical wiring.

Part B. The Dry Cell

CAUTION: Before beginning this procedure, be sure the DPDT switch is <u>not</u> 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 MnO_2 and saturated aqueous NH_4Cl.

3. Place the zinc plate on the wooden square. See Figure 5.

4. Wet a piece of filter paper with saturated aqueous NH_4Cl solution, place it on the zinc plate and tear off the overhanging edges. Obtain enough of the MnO_2 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.

Figure 5. Dry Cell

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_2 paste in the appropriate waste container. Clean the carbon block and the zinc plate by rinsing them in the beaker in the hood.

Part C. Other Electrochemical Cells

1. On the laboratory bench, there are two beakers and a U-tube salt bridge setup as shown in Figure 3 on p E21B-5. One beaker contains 1 M $CuSO_4$ and the other 1 M KNO_3. The salt bridge is also filled with 1 M KNO_3. (At the end of the experiment leave this setup just as you found it.)

2. Place the copper strip in the $CuSO_4$ solution and the aluminum strip in the KNO_3 solution. Connect the strips to different terminals of the voltmeter and observe the voltage. Record the voltage in the DATA SECTION.

3. Remove the aluminum strip from the solution and clean the strip by immersing it in NaOH solution in the 10-mL graduated cylinder until there is a vigorous evolution of hydrogen. Rinse the strip quickly with tap water and place it back in the KNO_3 solution.

   The following reactions take place when the aluminum strip is cleaned by NaOH.

$$Al_2O_3\,(s) + 3\,H_2O\,(\ell) + 2\,OH^-\,(aq) \rightarrow 2\,Al(OH)_4^-\,(aq)$$

$$2\,Al\,(s) + 6\,H_2O\,(\ell) + 2\,OH^-\,(aq) \rightarrow 2\,Al(OH)_4^-\,(aq) + 3\,H_2\,(g)$$

4. Measure the voltage again. Record this voltage in the DATA SECTION.

5. Replace the Al strip with the Zn strip and measure the voltage of the Cu-Zn cell. Record this voltage in the DATA SECTION.

Name _____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 21B

Part A. The Lead Storage Battery

Record the cell voltage of the lead storage battery: _____

Record the color of the $PbO_2(s)$ formed: _____

Part B. The Dry Cell

Record the original cell voltage of the dry cell: _____

Observations about the dry cell voltage:_____

_____

_____

_____

Part C. Other Electrochemical Cells

Record the voltage of the Cu-Al cell before cleaning: _____

Record the voltage of the Cu-Al cell after cleaning: _____

Record the voltage of the Cu-Zn cell: _____

Questions:

Part A. The Lead Storage Battery

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 PbO_2(s) to generate Cl_2 (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 Cl_2(g), $PbCl_2$(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.

Part B. The Dry Cell

1. Use equation (11) 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 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 12), what effect would this have on the recorded voltage? Explain your answer.

2. 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_4Cl(aq). Under these basic conditions, the products are ZnO(s) and Mn_2O_3(s). For this battery, write and balance the overall equation.

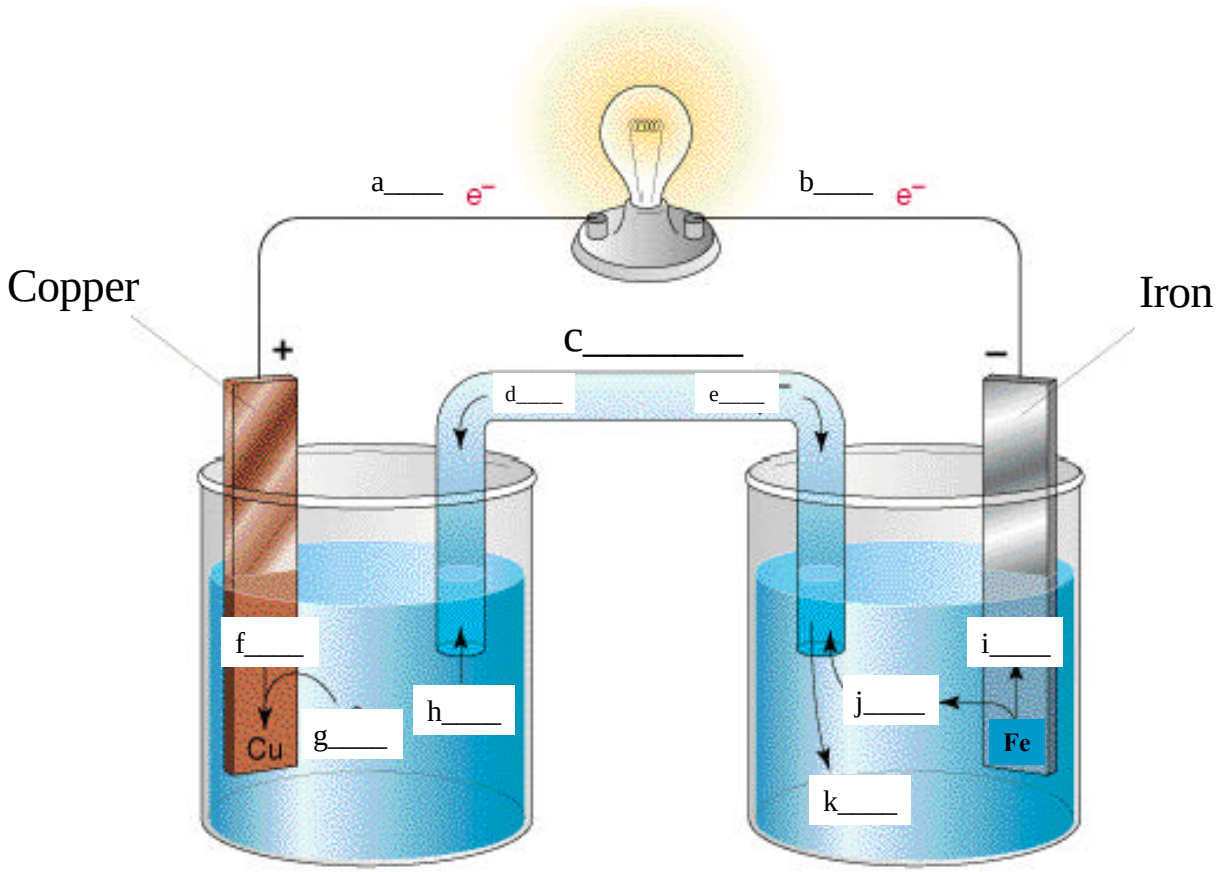
Part C. Other Electrochemical Cells

1. Explain any differences observed in the voltage before and after cleaning the Al strip.

2. Calculate the theoretical voltage that can be obtained from a Cu-Zn cell under standard conditions. Show your work.

3. In the Cu-Zn cell constructed in part C, do anions migrate toward the copper electrode or toward the zinc electrode? Explain your answer.

4. Using Figure 3 as a guide, fill in the blanks provided to label the following picture. Depicted is a Cu-Fe cell using a Na_2SO_4 solution in the connecting tube (name tube,'c'), a $CuSO_4$ solution in the copper beaker and a $FeSO_4$ solution in the iron beaker. Indicate the direction of the electron flow through the wiring (a, b) and show where electrons are used to reduce/oxidize Cu/Fe from/to solution.



Name _____ Section _____

Date _____

PRELAB EXERCISES
Experiment 21B

1. Identify the PbO_2 pole of the lead storage battery as the anode or cathode:

   (a) when discharging _____ (b) when charging _____

2. In terms of the chemical equations in the discussion for part A, explain the change in the density of the battery acid during discharge.

3. Write the balanced half-reactions and the overall reaction for the reduction and oxidation in the Cu-Al cell.

4. Write the balanced half-reactions and the overall reaction for the reduction and oxidation in the Cu-Zn cell.

5. A salt bridge is a vital part of the galvanic cells. Explain why the salt bridge is necessary.