

Experiment 21G

11/07/13

ELECTROCHEMISTRY: GALVANIC CELLS AND BATTERIES

MATERIALS: Ag, Cu, Zn strips; sandpaper; 0.25 M solutions of AgNO_3 , $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$; concentrated NH_3 ; plastic disposable pipets; DC power supply; various electrical leads; digital multimeter; paper strips for salt bridges; 1.5 M NaNO_3 ; 50 mL (3); $\text{MnO}_2(\text{s})$; saturated NH_4Cl solution; carbon block; square wooden block; zinc plate; filter paper; 400 mL beaker with 3.6 M H_2SO_4 ; Pb strips; double-throw switch; light bulb apparatus; low voltage motor.

PURPOSE: The purpose of this experiment is to illustrate the principles and practical aspects of galvanic cells and commonly used batteries.

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

1. Determine the half-reactions involved in spontaneous oxidation-reduction reactions.
2. Build galvanic cells and measure their electrical potentials and currents.
3. Draw schematic representations of cells, labeling electron flow direction, anode, cathode, and ion migration directions from salt bridges.
4. Explain the function of the lead storage and dry cell batteries.

PRE-LAB: Complete the Pre-Lab Assignment before coming to lab.

DISCUSSION:

General chemistry texts provide significant coverage for many aspects of electrochemistry, including the activity series, oxidation-reduction reactions, galvanic cells, and batteries. Some specific issues that are often not addressed as thoroughly in texts are discussed below:

Simple wiring diagrams. Electrochemistry involves simple electrical circuits, instruments for measuring electrical potentials and currents, electrodes, and external power supplies for pumping electrons through in certain directions, etc. Diagrams are used to depict these kinds of circuits and devices. Sophisticated diagramming conventions have been developed and will undoubtedly be used in later courses in physics and electrical engineering. The diagrams shown below are simple and are intended to mainly illustrate the connectivity of the various components of the circuits used in this experiment.

Simple galvanic cell circuit. Figure 1 depicts the simple circuit that allows for the determination of the electrical potential and/or current generated by a simple galvanic cell. The details of the electrodes are not included in this diagram.

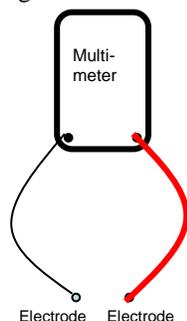


Figure 1. The wiring diagram for a simple galvanic cell connected through a multimeter. The electrodes may be such things as strips of metal immersed in solutions. The circuit is only completed if there is a way for electric current to flow between the electrodes, which is the reason that salt bridges are often required in such cells. As discussed below, the multimeter is capable of measuring either the electrical potential or the electric current generated by the cell. For the multimeters used in this experiment, when the electric potential reading is positive, the red wire will be attached to the cathode.

Circuits involving the double-throw switch. Figure 2 depicts two circuits which can be selected by throwing a special type of switch known as the double-throw switch. In the particular case shown, one of the circuits is a simple galvanic cell circuit, similar to that shown in Figure 1, and the other circuit is an electrolytic cell circuit, in which an external power supply pumps electrons in a certain direction. See the caption for a discussion.

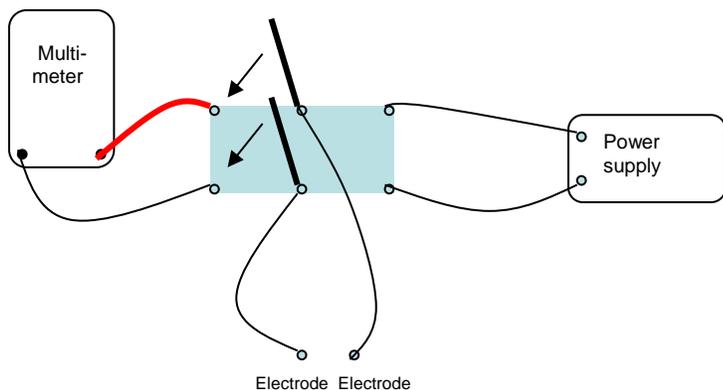


Figure 2. In this diagram, the double-throw switch is about to be closed towards the left. Once closed, the circuit will be identical to that in Figure 1. If the switch were thrown to the right, the circuit would include the power supply, as in an electrolytic cell. A multimeter can also be included in this right-hand circuit if one desires to monitor the electric current during electrolysis.

How multimeters work. Multimeters are electronic instruments which can measure several different electrical properties, e.g., electrical potential (voltage), current, and resistance. We will primarily be concerned with electrical potential and current in electrochemical applications.

When the multimeter is set to one of the voltage scales, it acts as a potentiometer. A potentiometer measures the voltage difference between two points of a circuit by creating an equal (but opposite) electromotive force and applying it to the circuit until the current is reduced to zero. Thus, when a multimeter is set to one of the voltage scales, there is no current flow, and the electrochemical process being investigated is actually stopped, even though the electric potential generated by the cell is measured. The standard unit for electrical potential is the volt, V.

When a multimeter is set to one of the current (amps) scales, the electrochemical process is not stopped by any opposing forces, as in the case when electrical potential is being measured. Instead, the current produced by the process is easily measured by applying appropriate physics principles, e.g., the relationship between electric current and magnetic fields. The standard unit for electric current is the ampere, which is defined as 1 coulomb of electric charge per second.

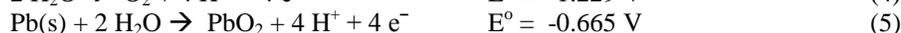
Passivation. Many metals, especially active metals, will react with components of the environment, e.g., oxygen gas in the air, to form a surface layer of metal oxide. In some cases, the layer is very tightly bound to the underlying pure metal, and may prevent further attack of the metal. This phenomenon is known as “passivation.” Aluminum, magnesium, and zinc all form passivating layers of oxides which provide varying degrees of protection to the underlying metal. Iron oxides, on the other hand, are not tightly bound to the underlying metal, and easily flake away and expose the underlying iron to further attack. Passivating layers of metal oxides are often very thin and can usually be removed by immersing the electrode in strong acid. Due to the amphoterism exhibited by aluminum, its passivating layer will also be removed by immersion in strong base. In many cases, the passivating layers can be removed mechanically through sanding. Some de-passivated metals, such as aluminum, reform the oxide layer very quickly due to the high reactivity of the metal with oxygen.

Real cells have real issues. General chemistry texts treat galvanic cells at an introductory level, without going into some of the details that are unavoidably associated with such cells. For example, varying degrees of efficiency in the motions of ions as they pass from the salt bridge into other cell compartments can reduce the effectiveness of the electromotive force, hence yielding measured voltages somewhat lower than expected. In addition, for those metals which tend to form passivating layers of metal oxides, the measured cell potentials are somewhat complicated, even if the bare metal has been exposed through sanding or some other chemical means, since the passivating layers tend to reform rather quickly. Even though the electrons can pass through ultra-thin passivating layers, the electrical potential generated in this situation is different than when the passivating layer is completely absent. The consequence of these kinds of complicating issues is that unless great care is taken to address them, the measured cell potentials will differ somewhat (generally, they will be lower) from those predicted by using the tabulated half-reaction potentials and the Nernst Equation.

Another issue that unavoidably affects measured electrical potentials is the ionic strength of the solutions in electrochemical cells. As has been noted in other experiments several times, ions in solution have an impact on the behavior of each other in such a way that the simple relationships often used in general chemistry are not precisely valid. This is especially true when ion concentrations are above 0.010 M. Some of the deviations of measured electrical potentials for cells can be attributed to these effects, especially when the concentrations of ions are in the 1 M range or higher, as is the case with many of the cells and batteries in this experiment.

Lead Storage battery. General chemistry textbooks provide detailed information about lead storage (also known as lead acid) batteries, and should be consulted in preparation for this experiment.

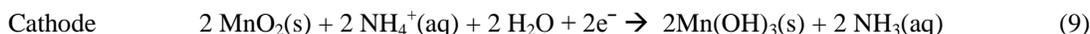
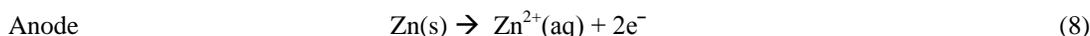
Most textbook discussions about lead storage batteries omit information about the process known as the “initial charging” of the battery. This is the process by which the lead storage battery is prepared for discharge, followed by recharging, processes which are discussed in detail in most texts. The “initial charging” process is simply the electrolysis involving two lead strips immersed in sulfuric acid. The strips are connected to an external power supply which pumps electrons from one strip to the other, forcing oxidation reactions to occur at the anode, and reduction reactions to occur at the cathode. Textbooks provide guidance about determining which of the possible redox reactions will likely occur at the anode and cathode during electrolysis. For the case of the lead storage battery undergoing “initial charging,” the candidate materials for oxidation include Pb(s) and H₂O, while candidate materials for reduction include H₂O and H⁺(aq). Standard reduction potential tables include reactions involving these materials, from which it is possible to select the likely anode and cathode reactions during electrolysis. For the “initial charging” of a lead storage battery, the possible anode reactions are:



The possible cathode reactions are:



Dry Cell battery. Unlike the lead storage battery, which is rechargeable, the dry cell is known as a primary cell (i.e., it cannot be recharged). This cell has a zinc cylinder as the anode and a carbon rod as the cathode. The carbon rod is surrounded by a paste formed by mixing solid MnO₂ with an aqueous solution of NH₄Cl. The zinc cylinder is kept separate from the paste by a porous paper, called the separator, so that there is no direct contact of the reactants associated with the anode and cathode. The electrode reactions are:



The function of the salt bridge is effectively performed as the Zn²⁺ ions migrate away from the anode, passing through the paper separator, and complex with the NH₃ produced at the cathode, forming Zn(NH₃)₂²⁺. In this way, charge balance is maintained in both the anode and cathode regions of the cell, and neither product builds up concentration near the electrode where they are produced, which would, according to the Nernst Equation, quickly diminish the cell’s electrical potential. The porous separator only allows the dissolved aqueous ions to pass through, keeping the Zn(s) and the MnO₂(s) from coming into direct contact. The product written as manganese(III) hydroxide is actually a complicated hydrated species, which is sometimes written as Mn₂O₃(s) + 3H₂O(l), as in your textbook.

PROCEDURE:

Part A. Activity Series and Simple Galvanic Cells

1. Your instructor will demonstrate the setup of a galvanic cell, including the simple paper salt bridge, the use of the double-throw switch, and the use of the digital multimeter (also see the instruction sheet on p. 9). He or she will also discuss the need for removing oxide layers from the underlying metals (e.g., via sanding) before use in electrochemical applications. Make any notes for future reference, if needed.
2. Add 5.0 mL of 0.25 M Cu(NO₃)₂ to a small beaker; 5.0 mL of 0.25 M Zn(NO₃)₂ to a second small beaker and 5.0 mL of 0.25 M AgNO₃ to a third. Clean the Cu and Zn metal strips by sanding, and rinse off any metal or sandpaper dust with distilled water. One at a time, immerse the clean strips of Cu metal, Zn metal, and Ag metal in each solution for about 30 seconds (or less if there are obvious signs of reaction). Remove the metal strips and use the data sheet to record any changes to them or to the solutions. Sand off any discolored areas on the metal strips after each test.

✎ Answer in-lab questions #1 and #2 on page 8.

3. Using the three spontaneous reactions observed in Step 2 as a guide, set up a galvanic cell for each (or for specific ones if directed by your instructor). The general setup was described earlier by your instructor. Each half-cell should consist of a cleaned metal strip and a beaker containing 10.0 mL of the corresponding 0.25 M metal ion solution. (i.e., a metal is always placed in a solution of its own metal ion.) Use a fresh paper salt bridge (soaked with NaNO_3 solution) for each. Attach the digital multimeter such that the voltage is a positive value. Use the data sheet to record the voltage (emf) as measured by the digital multimeter for each, and to record which lead is attached to which metal.

✎ Answer in-lab question #3 on page 8.

4. Make a new galvanic cell based on the Cu/Zn system, using 10.0 mL of the 0.25 M solutions and the appropriate metal strips in each half-cell as before. Measure and record the voltage (emf) of this cell, on the data sheet.

✎ Answer in-lab question #4 on page 8.

5. Add 10.0 mL of distilled water to the Zn^{2+} solution. Measure and record the new voltage. Replace the liquid in the zinc half-cell with 10.0 mL of fresh Zn^{2+} solution, and insert a new paper salt bridge. To the Cu^{2+} solution, add a few crystals of solid CuSO_4 . Measure and record the new voltage. Replace the Cu^{2+} solution and the salt bridge. Add a few drops of concentrated NH_3 solution to the Cu^{2+} solution, recording observations of evidence for any reactions. (What reaction takes place between Cu^{2+} ions and ammonia?) Measure and record the new voltage.

✎ Answer in-lab question #5 on page 9.

Part B. Batteries

Lead Storage Battery

1. In the instructor's hood, carefully clean two lead strips with sandpaper. Make sure the lead shavings go into the proper waste container, and avoid inhaling the lead dust. Place the two lead strips on opposite sides of the 400 mL beaker which contains 3.6 M H_2SO_4 , found in your hood. Make sure the lead strips do not touch each other.

2. Using the double-throw switch, connect the power supply, the lead strips, and the digital multimeter in such a way that the switch can be set to either include or exclude the external power supply at any given time. Remember, it will be needed during the initial charging and recharging phases of operation, but not during the discharging phase. See Figure 3 for a simple illustration of this type of circuit; compare with the circuits in the Discussion section. (The light bulb and motor will be used at a later time; do not connect them yet.) Verify with your instructor that your setup is correct.

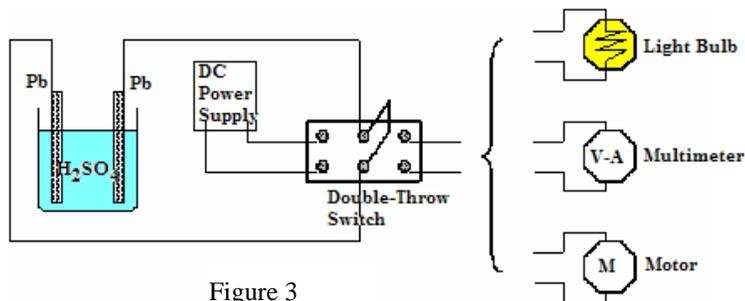


Figure 3

3. Flip the switch and perform the initial charging of the battery by applying the external power supply at 12V for about 5 minutes. Record any observations of changes to the metals or the solution.

✎ Answer in-lab question #6 on page 9.

4. Flip the switch and use the digital multimeter to measure the electrical potential generated by the lead storage battery. Note that the power supply should NOT be in the circuit, since this is a spontaneous (galvanic) cell after it is charged.

5. Disconnect the multimeter and insert the light bulb apparatus into the battery circuit. Try to power the bulb with your battery. Then remove the light bulb from the battery circuit and replace it with the small motor. See if your battery will power the motor. Which device requires less power to run? Remove the motor from the circuit. Record your observations on the data sheet.

6. Recharge the battery for 2 minutes. Measure and record the voltage after recharging. Allow the battery to discharge for 20 seconds by switching to a current setting, and then measure the voltage again. (Remember that the

battery is only able to discharge when the digital multimeter is set to one of the amperage scales.) Repeat the discharge/voltage measurement sequence again 5-6 more times (or more if directed by your instructor), using 20 second discharge periods. Record the measurements on the data sheet. An important property of a lead-acid battery is the way it maintains its voltage until close to the end of its life.

7. Disassemble the lead storage battery, but **DO NOT DISCARD THE 3.6 M H₂SO₄**. Leave the 400 mL beaker containing the 3.6 M H₂SO₄ in your hood, for use by the next laboratory section.

Dry Cell Battery (Your instructor may construct this cell as a demonstration, or have you construct it.)

1. Using the double-throw switch, attach the leads to the zinc plate (anode) and the carbon block (cathode). Include the digital multimeter in the circuit so that the electrical properties of the cell can be measured. See the Discussion section for a simple diagram of such a circuit. You do NOT need the power supply for this cell.
2. On the wooden block, place the following (in sequence): (1) the zinc plate; (2) a piece of filter paper saturated with NH₄Cl solution (the separator); (3) a paste consisting of MnO₂ and NH₄Cl (obtain from your instructor; handle this paste with caution, since the MnO₂ stains both hands and clothes); and (4) the carbon block.
3. Use the data sheet to record the voltage generated by this dry cell. Sometimes, the voltage can be increased by improving the contact of the various materials in the cell. This can be done by pressing down on the carbon block with some non-conducting material, e.g., a beaker (caution: pressing too hard will break the carbon block).
4. Measure and record the current produced by the cell. Test to see if your battery will light the light bulb or run the motor, and record your observations.

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DATA SECTION
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PART A

Step A.2 Record your observations:

METAL	ION	RXN?	Observation	METAL	ION	RXN?	Observation
Ag	Cu ²⁺			Ag	Zn ²⁺		
Cu	Ag ⁺			Cu	Zn ²⁺		
Zn	Ag ⁺			Zn	Cu ²⁺		

Step A.3 Record data below for two galvanic cells

Cell: _____ Voltage: _____ Anode: _____ Cathode: _____

Cell: _____ Voltage: _____ Anode: _____ Cathode: _____

Step A.4 Record data below for the Zn/Cu cell

Cell: _____ Voltage: _____ Anode: _____ Cathode: _____

Step A.5 For changes to the Zn/Cu half-cell compartments

- Addition of distilled water New voltage: _____
- Addition of CuSO₄ solid New voltage: _____
- Addition of concentrated NH₃ New voltage: _____

Observations of color change : _____

PART B

Step B.3 Record observations for the INITIAL CHARGE of the Pb-acid battery

Bubbles at the anode (yes or no) _____ Identify gas: _____

Bubbles at the cathode (yes or no) _____ Identify the gas: _____

Coating formed on the anode (yes or no) _____ cathode (yes or no) _____

What is the chemical formula of the coating? _____

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DATA SECTION
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Step B.4 Voltage of Pb-acid battery

Voltage: _____

Step B.5 Record observations for fan and motor

Observations: _____

Step B.6 Record voltage for Pb-acid battery

Total Discharge time (s)	Measured Voltage (mV)

Dry-cell battery Steps 3 & 4

Voltage reading: _____ Red wire is attached to which material: _____

Current reading: _____

Observations: _____

DATA ANALYSIS (Pb-acid battery):

Use Excel to make a graph showing the measured voltage vs. discharge time for the lead storage battery. Use the data from Part B, step 6. Attach the spreadsheet with graph to your lab along with a short discussion of your data. In particular, address the question of why car batteries seem to fail without warning.

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✎ **IN-LAB QUESTIONS** ✎
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PART A

1. For any combination of metal plus solution where there were indications of spontaneous reactions, write the corresponding balanced reactions. Verify with your instructor that you have correctly identified these reactions.

2. Based on your results, order the three metals in terms of their reactivity (i.e., activity). Are the observed spontaneous reactions consistent with your knowledge of the activity series? Verify with your instructor that your conclusions are correct.

most active metal _____ > _____ > _____ least active metal

3. Draw schematic diagrams of the galvanic cells, including labels for the direction of electron flow, migration of ions from the salt bridge, and anode and cathode. Simple examples of such diagrams can be found in any general chemistry text. Verify with your instructor that your diagrams are correct.

4. The potential provided by a galvanic cell is described by the Nernst equation, which is discussed in detail in your textbook. For the Cu/Zn cell it is:

$$E = 1.10V - \frac{0.0592V}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad (\text{at } 25^{\circ}\text{C})$$

Predict the effect on the cell potential E when the following changes are made to your cell. How will E change if you:

a) add 10 mL of distilled water to the beaker with the Zn^{2+} solution? decrease no change increase

b) add $CuSO_4(s)$ to the beaker with the Cu^{2+} solution? decrease no change increase

c) add conc. $NH_3(aq)$ to the beaker with the Cu^{2+} solution? decrease no change increase

5. Compare your observations to the predictions you made in question 4 above. Use the Nernst equation to explain your observations. Verify with your instructor that your analysis of these effects is correct.

PART B

6. How are your observations consistent with the reactions occurring during this initial charging process? (See the candidate electrolysis reactions mentioned in the Discussion section.) Which reaction occurs at the cathode, and which one occurs at the anode? Which pole of the power supply is associated with each?

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POST-LAB QUESTIONS

1. If Mg metal and 0.25 M $\text{Mg}(\text{NO}_3)_2$ solutions were coupled in a half-reaction with the Cu/Cu^{2+} system, which metal would serve as the anode? Use the Nernst equation to calculate the expected electric potential generated by the cell.

2. Diagram the cell described in question 1, indicating the anode and cathode, concentrations in the two solutions, directions of ion and electron flows, etc.

3. Explain what happens when a “dead” lead storage battery is connected to another battery (e.g., when jump-starting a car with jumper cables). Why is it important to connect the cables to the correct terminals (i.e., electrodes)? Why must the car with the good battery be left running?

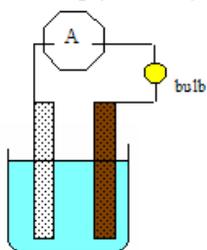
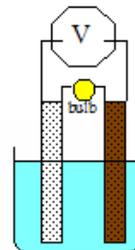
4. How would the voltage of a dry cell be affected if the Zn^{2+} ions simply built up near the Zn plate anode?

5. Dry cells are related to alkaline batteries, where the reactants are also $\text{Zn}(\text{s})$ and $\text{MnO}_2(\text{s})$. However, the electrolyte solution for alkaline batteries is $\text{NaOH}(\text{aq})$ instead of $\text{NH}_4\text{Cl}(\text{aq})$. The products of the half-reactions are $\text{ZnO}(\text{s})$ and $\text{Mn}_2\text{O}_3(\text{s})$, respectively. Write and balance the overall reaction for alkaline batteries.

USE OF THE TENMA DIGITAL MULTIMETER

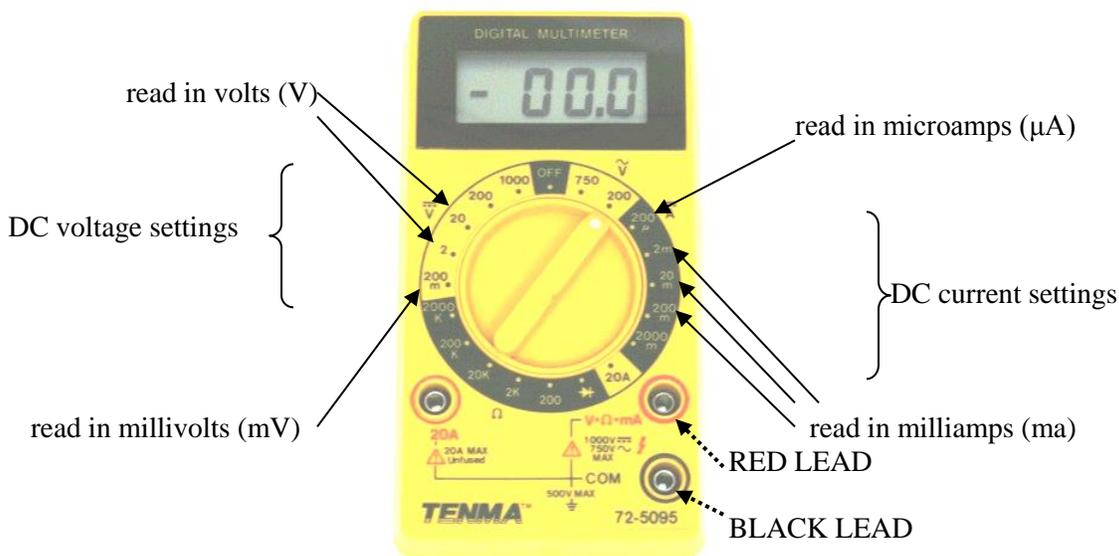
As described in the discussion, a multimeter can measure several important electrical properties, namely voltage, current and resistance. We will only be interested in the first two for this experiment. Because the instrument functions differently for these different measurements, it is important that it be set up properly to make them. Because it has multiple scales in each case, it is also important that you read it properly to get meaningful data. This sheet provides a brief description of proper use of the device.

Making Voltage Readings As discussed earlier, when the multimeter is set to one of the voltage scales, it acts as a potentiometer. This measures the voltage difference between two points of a circuit by creating an equal (but opposite) electromotive force and applying it to the circuit until the current going through the meter is reduced to zero. Thus, when a multimeter is set to one of the voltage scales, there is no current flow in the meter, and the electrochemical process being investigated is actually stopped. What you read is based on the voltage that was applied to stop current flow. For this to work properly, the two leads of the meter must be placed ACROSS the circuit, touching the two points of interest (usually the electrodes). See the drawing at right. Also, note that the red wire is attached to the cathode when the voltmeter displays a positive value. Make your connections to get positive voltages; knowing which electrode is the cathode will help you analyze the chemical behavior of the system.



Making Current Readings When a multimeter is set to one of the current (amps) scales, the electrochemical process is not stopped by any opposing forces, as in the case when electrical potential is being measured. Instead, the current produced by the process is passed through the meter where it is measured. Thus for current readings, the meter must be IN the circuit. See the drawing at left.

Reading Values of Voltage or Current Because there are different scales on the meter, and even different units within the voltage scales or current scales, it is essential that you note what position you set the dial to, and to always include the units with your readings. Shown below is an image of the meter face. The label at each setting (e.g. 200m) indicates the maximum reading on that scale.



Here are some general rules for reading the meters. Follow these to get consistent results.

1. Always write down the UNITS with your values.
2. **Always use the LOWEST setting that gives a meaningful reading**, because it will provide the greatest precision and accuracy. When reading voltage, start with the 200m scale, and then go up. (You will never need the 200V or 1000V settings!) When reading current, start with the 200 μ scale, and then go up. (You will never need the 2000m scale!) **NOTE:** If the voltage or current were completely unknown, you would probably start with a high scale, and go down to the lowest with a good reading, in order to protect the meter. That will not be a problem here.
3. If the meter simply shows a constant number "1" on the left side of the display, you are off-scale. Go to the next higher scale.

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**Pre-Lab Exercises
Experiment 21G**

1. Based on the discussion of multimeters and circuits, answer the following questions:

a. For all operations in the lab, you should connect the multimeter such that it reads positive values. When the multimeter is correctly connected in that way, the red wire of the meter will be attached to the:

- i. salt bridge ii. ground iii. anode iv. cathode

b. Select ALL that apply: When the multimeter is set to a voltage scale

- i. the electrochemical process occurs
ii. the electrochemical process does not occur
iii. current flows through the circuit of interest
iv. current does not flow through the circuit of interest.

c. Select ALL that apply: When the multimeter is set to a current (or amp) scale

- i. the electrochemical process occurs
ii. the electrochemical process does not occur
iii. current flows through the circuit of interest
iv. current does not flow through the circuit of interest.

2. According to the activity series (p. 143 in the Chang text), which of the following reactions from each pair SHOULD occur?

- a. $\text{Cu(s)} + \text{Pb(NO}_3)_2\text{(aq)}$ or $\text{Pb(s)} + \text{Cu(NO}_3)_2\text{(aq)}$
b. $\text{Al(s)} + \text{Cr(NO}_3)_3\text{(aq)}$ or $\text{Cr(s)} + \text{Al(NO}_3)_3\text{(aq)}$
c. $\text{Zn(s)} + \text{AgNO}_3\text{(aq)}$ or $\text{Ag(s)} + \text{Zn(NO}_3)_2\text{(aq)}$

d. Write out the balanced net ionic equation for the correct reaction in part (c) above. (You will use this one in lab.)

3. Write the half-reactions which occur when a lead storage battery is undergoing initial charging, discharging, and recharging. (Hint: read the introduction to this lab and your textbook.)

Initial Charging:

Discharging:

Recharging: