

Experiment 21B

01/13/2020

THE ACTIVITY SERIES AND ELECTROCHEMICAL CELLS

MATERIALS: Four 50 mL beakers; 10 mL graduated cylinders (3); glass marking pen; stirring rod; plastic dropper; stainless steel spatula; voltmeter/ohmmeter; alligator clips; 1 cm x 13 cm filter paper strips; strips of metals (Cu, Zn); Ag wire; 0.25 M solutions of $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ and AgNO_3 ; 1.5 M NaNO_3 solution; concentrated $\text{NaOH}(\text{aq})$ solution (dropper bottle); solid CuSO_4 , sandpaper; (also for demo: Fe nail, Fe^{2+} or Fe^{3+} solution, 3 M HCl)

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.

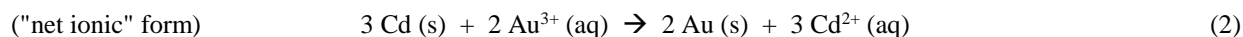
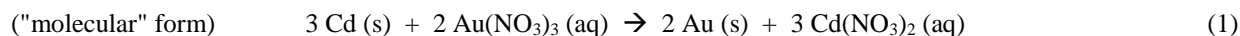
LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Write an electrochemical Activity Series based on experimental observations.
2. Define the following terms: oxidation, reduction, oxidizing agent, reducing agent, electrochemical activity series, electrode, electrolyte.
3. Explain the use and purpose of a salt bridge.
4. Identify an electrode as either a cathode or an anode, and identify directions of electron and ion flow in a spontaneous electrochemical cell.
5. Write the half reaction occurring at each electrode and a complete balanced overall reaction for an electrochemical cell.
6. Use the Nernst equation to understand the effects of changing conditions on the cell voltage.

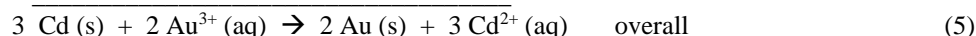
DISCUSSION:

For oxidation-reduction (redox) reactions, reactivity depends on 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*). In this experiment, we will compare the behavior of several metals to create a list called the “activity series”, which can be used to predict reactions in many electrochemical processes. These same spontaneous redox reactions can also be utilized as electrochemical cells (or batteries), and we will construct and examine several such cells.

For metals that do not react with water a simple way to determine the relative redox reactivities 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:



It is clear that this is a redox reaction because cadmium metal loses electrons (is oxidized) to form Cd^{2+} , while gold(III) ions are reduced (gain electrons) to form metallic gold. The half-reactions are:



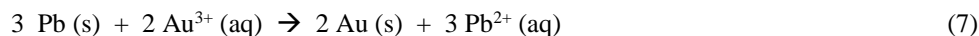
Experimentally, it is observed that the cadmium dissolves, while a layer of gold metal plates out on the remaining cadmium. Experiments also indicate that the reverse reaction, between metallic gold and dissolved cadmium ions, does not occur:



Gold does not displace cadmium from cadmium nitrate. These observations of reactions (5) and (6) mean that cadmium is a more active metal (more willing to lose electrons) than is gold. Since Cd is more easily oxidized than Au, it ranks above Au in the activity series:

| | |
|-----------------------------|----|
| Activity series, version 1: | Cd |
| | Au |

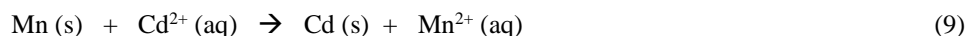
Testing other metals allows us to broaden the list. For example, we find that lead will displace gold metal from a gold compound, but will *not* displace cadmium metal from a cadmium compound:



That means that lead must be more active than gold, but less active than cadmium, so our revised activity series is

| | |
|-----------------------------|----|
| Activity series, version 2: | Cd |
| | Pb |
| | Au |

Suppose we ran the reaction between Mn metal and Cd²⁺ ions, and formed Cd metal?



Where would that place the manganese on the activity series? What would you predict for the reaction between cadmium metal and manganese ions? (Think about it and answer in the Pre-lab.)

By a similar set of reactions, you will establish the relative ease of oxidation for copper, silver and zinc metals. The activity series has predictive power - any metal on the list is able to displace the elements *below it* from their compounds by a spontaneous redox reaction. More generally, **the reduced form (the metal) of an element on the activity list will react spontaneously with the oxidized form (the ions) of any element lower on the list.**

Since spontaneous reactions occur between a metal and the dissolved ion of a second metal, ΔG for the reactions must be negative; that also means that there was energy available to do work. An electrochemical cell is a device constructed so 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 to a light bulb, motor, etc., and 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. The two metal rods in the cell are called *electrodes*. Cd is the *anode*, the electrode where oxidation occurs. 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. The negative electrons move from the negative anode towards the gold cathode, so it must be positive. This convention (+ for cathode and - for anode) is true for all spontaneous electrochemical cells. The other new feature in the cell figure is the inverted U-tube, called a *salt bridge*, connecting the two beakers (half-cells). The salt bridge completes the electrical circuit by allowing ions (not electrons) to carry charge between the half-cell solutions. The salt bridge contains non-reactive ions that equalize charge by the flow of cations towards the cathode and anions towards the anode. This is necessary because ions produced or consumed at the anode and cathode, respectively (reactions 3 and 4), would otherwise create a charge imbalance that would halt the process.

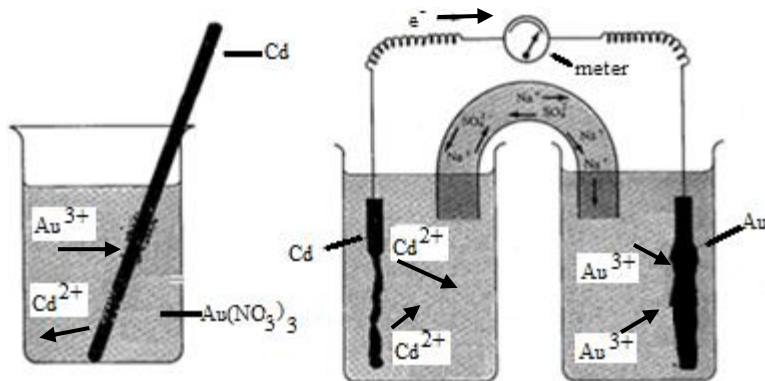


Figure 1. Spontaneous Electrochemical Reactions

The force needed to move the electrons through the external circuit is called the electromotive force (emf), which has units of volts (V). It is the difference in electrical potential between the half-cells and is also known as the voltage. Just as the complete cell can be treated as two half-cells, the potential difference can be treated as the difference between two half-cell potentials. These half-cell potentials are typically reported at 25°C and 1 M (or 1 atm for gases) and are referred to as standard reduction potentials, E° .

The activity series summarizes the relative ease of oxidation of metals. The related Table of Standard Reduction Potentials permits calculation of cell potentials. For these species, the table would be:

| Reduction Half-Reaction | Std. Reduction Potential @ 25°C (V) |
|--|-------------------------------------|
| $\text{Au}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Au}(\text{s})$ | 1.50 |
| $\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Pb}(\text{s})$ | -0.126 |
| $\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cd}(\text{s})$ | -0.403 |

Here the half-reactions are all written as reductions, with the most easily reduced species (Au^{3+}) at the top left. The oxidations we have been describing are the reverse of the reactions written in this table, so the most easily oxidized species (Cd) is at bottom right. (If you just look at the right sides of the reactions, it is the activity series, upside down.) Spontaneous reactions can be predicted by the diagonal rule – **a substance high on the left side of the table will react spontaneously with a substance lower than it, but on the right side.** For a cell made from that spontaneous reaction, the half-reaction higher up will be the cathode half-reaction, and the reverse of the lower one will be the anode half-reaction. The cell potential under standard conditions E°_{cell} at 25°C can then be calculated as

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad (10)$$

where E°_{cathode} and E°_{anode} are the standard reduction potentials for the half-reactions occurring in the cathode and anode, respectively. Values of the half-cell potentials are taken from the table above. For the Au/Cd cell, that value would be $E^\circ_{\text{cell}} = 1.50 \text{ V} - (-0.403 \text{ V}) = 1.90 \text{ V}$. Under non-standard conditions, the cell potential E can be calculated with the Nernst equation

$$E = E^\circ - \left(\frac{RT}{nF}\right) \ln Q \quad (11)$$

where R is the gas constant (8.314 J/mol K), T is the Kelvin temperature, n is the number of moles of electrons transferred, and F is the Faraday constant (96485 C/mol e^-). Q is the reaction quotient, familiar from the discussion of equilibrium.

PROCEDURE:

Demonstration – Your instructor may demonstrate the overall approach to the lab, using iron and copper metals, and solutions containing iron ions or copper ions. Record your observations of the demonstration on the Data Page, and take note of how the cell is set up.

Part A. Reactions of Metals with Metal Ion Solutions – the Activity Series

1. Thoroughly rinse the three 10 mL graduated cylinders with deionized water. Label one of them for use ONLY with Cu ion solutions, one for use ONLY with Zn ion solutions, and one for use ONLY with Ag ion solutions.

2. Using the proper graduated cylinders, add 5.0 mL of 0.25 M $\text{Cu}(\text{NO}_3)_2$ to a small beaker; 5.0 mL of 0.25 M $\text{Zn}(\text{NO}_3)_2$ to a second small beaker and 5.0 mL of 0.25 M AgNO_3 to a third. Clean the Cu and Zn metal strips by sanding *lightly*, 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 record any changes to them or to the solutions. Sand and rinse off any discolored areas on the metal strips after each test.

☒ Answer in-lab questions #1 and #2 on page 5.

Part B. Construction of Electrochemical Cells

1. Using the three spontaneous reactions observed in Step 1 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 5.0 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 strip of filter paper soaked in NaNO_3 solution as a salt bridge; the ends must be immersed in the *liquid* of each beaker. (Use a fresh salt bridge for each cell that you make.) Attach the digital multimeter such that the voltage is a **positive** value. Record the voltage (emf) as measured by the digital multimeter for each and record which wire is attached to which metal.

☒ Answer in-lab question #3 on page 6.

Part C. Further Examination of a Cell

1. Make a new galvanic cell based on the Cu/Zn system, using 5.0 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.

2. Two conductors are necessary for any cell, but only one of the specific metals (Cu or Zn) is required to make this cell work. Find out which by replacing each electrode (one at a time) with a metal spatula. Essentially no voltage will be measured when the critical electrode is replaced by a spatula. Which is it?

☒ Answer in-lab question #4 on page 7.

3. Restore both Cu and Zn electrodes and measure the cell voltage. Add a few drops of 6.0 M $\text{NaOH}(\text{aq})$ near the Cu(s) electrode. Measure and record the new voltage immediately after adding the $\text{NaOH}(\text{aq})$. Now, add a few drops of 6.0 M $\text{NaOH}(\text{aq})$ near the Zn(s) electrode. Measure and record the new voltage immediately after adding the $\text{NaOH}(\text{aq})$.

☒ Answer in-lab question #5 on page 7.

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. Rinse all glassware with deionized water.

Name _____

Section _____

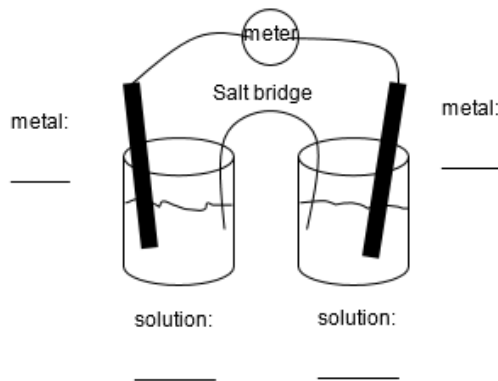
Partner _____

Date _____

DATA SECTION AND IN-LAB QUESTIONS
Experiment 21B

Instructor Demonstration

| Demonstration Reaction | | | |
|------------------------|------------------|------------|--------------|
| Metal | Metal Ion | Rxn? (Y/N) | Observations |
| Cu | Fe ²⁺ | | |
| Fe | Cu ²⁺ | | |



Cu/Fe: Voltage _____

Red wire attached to _____

Anode is _____ Cathode is _____

½ rxn at anode is _____ ½ rxn at cathode is _____

Part A. Data: Reactions of Metals with Metal Ion Solutions

| Reactions with Metal Ion #1 | | | |
|-----------------------------|------------------|------------|--------------|
| Metal | Metal Ion | Rxn? (Y/N) | Observations |
| Ag | Cu ²⁺ | | |
| Cu | Ag ⁺ | | |
| Zn | Ag ⁺ | | |

| Reactions with Metal Ion #2 | | | |
|-----------------------------|------------------|------------|--------------|
| Metal | Metal Ion | Rxn? (Y/N) | Observations |
| Ag | Zn ²⁺ | | |
| Cu | Zn ²⁺ | | |
| Zn | Cu ²⁺ | | |

IN-LAB QUESTIONS

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). Verify with your instructor that your conclusions are correct.

most active metal _____ > _____ > _____ least active metal

Part B. Construction of Electrochemical Cells

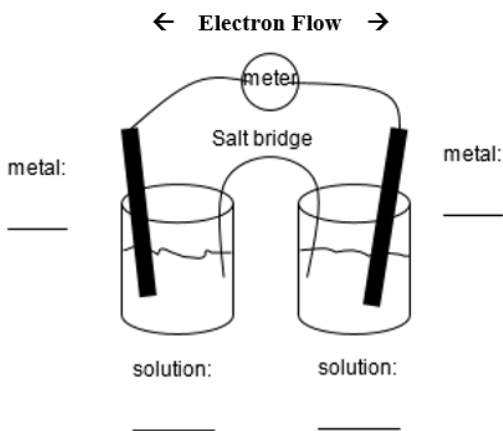
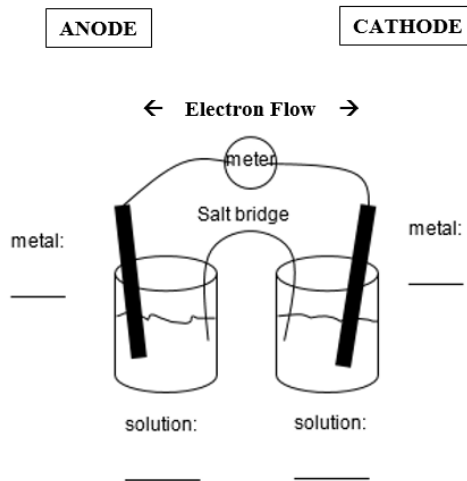
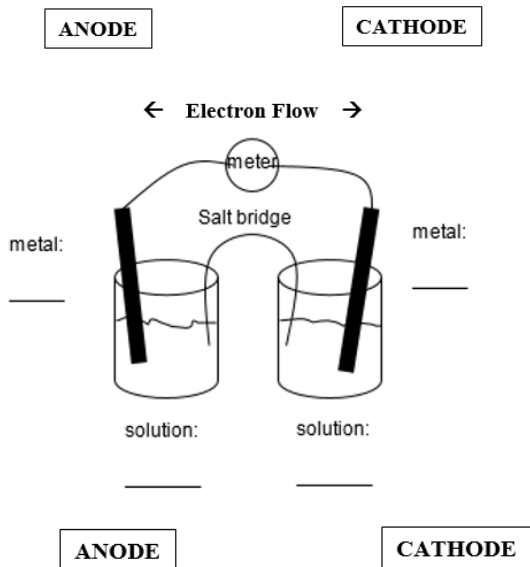
Data: Combinations of metal plus metal ion solution that gave spontaneous reactions:

| | Metal | Metal Ion Solution | Voltage (V) | Negative Electrode (Anode) |
|---|-------|--------------------|-------------|----------------------------|
| 1 | | | | |
| 2 | | | | |
| 3 | | | | |

Instructor's Initials _____

IN-LAB QUESTIONS

3. Draw schematic diagrams of the galvanic cells, including labels to identify the metals of the cathode and anode and metal ions in the cathodic and anodic beakers, and circling the correct direction of electron flow. Also identify the direction of migration of ions from the salt bridge. Verify with your instructor that your diagrams are correct.



In each cell, the ions of the salt bridge flow towards the anode or cathode electrodes as:

Na^+ flows towards the _____.

NO_3^- flows towards the _____.

Part C. Further Examinations of a Cell – Steps 1 and 2.

DATA:

Original cell voltage of Cu-Zn cell for Part C _____

Cell voltage for Cu-spatula cell for Part C _____

Cell voltage for Zn-spatula cell for Part C _____

✂ IN-LAB QUESTIONS ✂

4. Which electrode is required to provide any potential for this cell? _____

Part C. Further Examinations of a Cell – Steps 3.

| Cell | Voltage (V) |
|--|-------------|
| Starting Cu/Zn cell | |
| Cu/Zn cell after NaOH addition to Cu half-cell | |
| Cu/Zn cell after NaOH addition to Zn half-cell | |

Chemical Observations:

NaOH(aq) to Cu half cell:

NaOH(aq) to Zn half cell:

✂ IN-LAB QUESTIONS ✂

5. 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:

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

Based on the equation, explain the effect on the cell potential E when the NaOH(aq) was added to:

Cu²⁺(aq) solution :

Zn²⁺ (aq) solution:

POST-LAB QUESTIONS
Experiment 21B

1. Part of the table of standard reduction potentials is provided here:

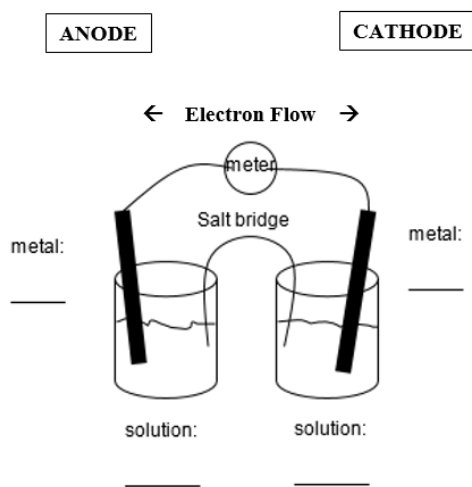
| Reduction Half-Reaction | Std. Reduction Potential @ 25°C (V) |
|--|-------------------------------------|
| $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightarrow \text{Cu}(\text{s})$ | 0.337 |
| $\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightarrow \text{Mg}(\text{s})$ | -2.37 |

a. Which metal will be higher on the activity series?

b. Write out the net ionic reaction for the spontaneous process that will occur involving the species $\text{Cu}(\text{s})$, $\text{Cu}^{2+}(\text{aq})$, $\text{Mg}(\text{s})$ and $\text{Mg}^{2+}(\text{aq})$.

c. What is the standard cell potential E° at 25°C for this process?

d. Complete the blanks to diagram the cell. Also identify the direction of electron flow (circle) in the external wire.



1. If Mg metal and 0.25 M $\text{Mg}(\text{NO}_3)_2$ solutions were coupled with Cu metal and 1.00 M $\text{Cu}(\text{NO}_3)_2$ solution in constructing the cell, what would be the cell potential E at 25°C?

Name _____

Section _____

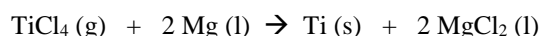
Date _____

**Pre-Lab Exercises
Experiment 21B**

1. When metal atoms form cations they (circle):

- a. lose electrons and are oxidized
- b. lose electrons and are reduced
- c. gain electrons and are oxidized
- d. gain electrons and are reduced.

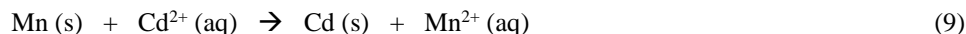
2. The following displacement reaction is used commercially to obtain the strategically important metal titanium.



Based on this reaction (circle)

- a. Magnesium is the more active element and undergoes oxidation.
- b. Magnesium is the more active element and undergoes reduction.
- c. Titanium is the more active element and undergoes oxidation.
- d. Titanium is the more active element and undergoes reduction.

3. In the Discussion section you were given equation (9)



and asked where that result places manganese on the activity series that was developed in the Discussion. Choose the correct order, listed from most active to least active.

- a. Au > Pb > Cd > Mn
- b. Cd > Mn > Pb > Au
- c. Mn > Cd > Pb > Au
- d. Au > Cd > Mn > Pb

4. Based on the reaction of equation (9), what would you predict for the reverse reaction, between Cd metal and Mn^{2+} ions?

- a. the reaction will occur spontaneously
- b. the reaction will not occur spontaneously
- c. the reaction will lead to formation of Mn^{4+} ions
- d. the results cannot be predicted

5a. Iron is above copper on the activity series. Based on that fact, write the net ionic equation expected for a spontaneous reaction involving Fe(s), Cu(s), $\text{Fe}^{2+}(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})$.

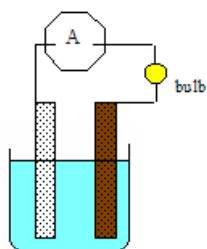
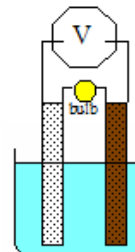
5b. If an electrochemical cell were made with the components described above, what would be the metal and metal ion in the cathodic half-cell?

metal: _____ metal ion: _____

USE OF THE DIGITAL MULTIMETER

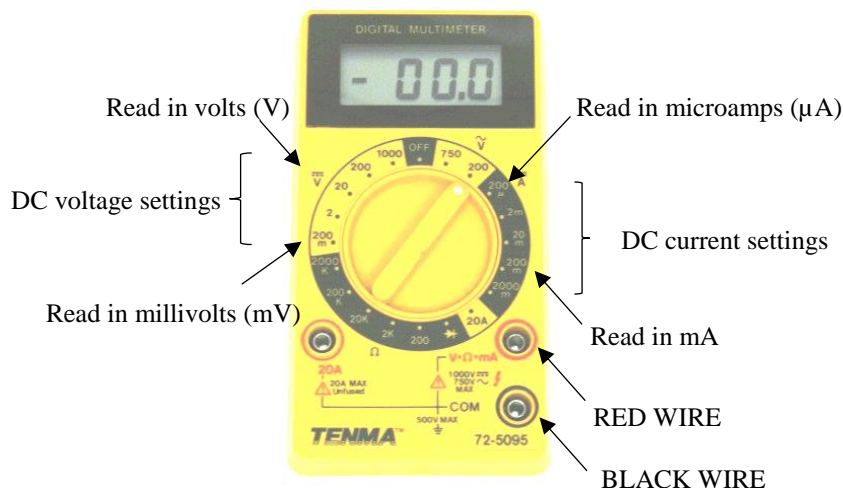
A multimeter can measure several important electrical properties, namely voltage, current and resistance. We will only be interested in the first two for this experiment. Because the instrument functions differently for these different measurements, it is important that it be set up properly to make 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 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 under investigation 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. For the **TENMA** multimeter, 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!). 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.
3. For the **EXTECH** multimeter, when reading voltage, use the V_{DC} setting. The instrument will adjust the scale automatically. When reading current, start with the μ A setting, if needed you can go to the next higher scale (mA). If "OL" appears in the display during a measurement, you are off-scale. Go to the next higher scale.