8 Electrochemistry: Oxidation-Reduction

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- **Observe several different oxidation and reduction reactions and identify oxidizing and reducing agents.**
- **Produce a reduction potential series with half-reactions arranged in order with the strongest oxidizing agents at the top.**
- **Measure the voltages of simple electrochemical cells.**

DISCUSSION

In this experiment, you will measure the oxidizing and reducing strengths of four metals—zinc (Zn), copper (Cu), magnesium (Mg), and iron (Fe)—in two independent ways.

In the first part, you will measure the voltage of electrochemical cells made from these metals and their ions. You will identify the different components of the cells, such as the anode and the cathode. And you will write the equations for the half-reactions and the complete reaction of each cell.

Half-reactions or half-cells are the imaginary parts of the total reaction that consider either the oxidation (loss of electrons) alone or the reduction (gain of electrons) alone. For example, the half reaction for the reduction of silver ions to silver metal is written

$$Ag^{+} + e^{-} \rightarrow Ag(s)$$

A half-reaction cannot occur by itself; it must be coupled with or added to another half-reaction to give a complete reaction. For this reason, the voltage of a half-cell cannot be measured. Nevertheless, a relative voltage or potential can be assigned to each half-cell. These assigned voltages have two properties. First, the sum of two half-cell voltages must equal the (measurable) voltage of the corresponding complete cell. Second, their values must be relative to the arbitrarily-chosen voltage of some reference half-cell. (A list of such voltages for standard reduction half-cells, which are called ***standard reduction potentials***, is given in Appendix J of your textbook.) You will assign relative voltages to each of the four reduction half-cells of this experiment, and arrange them from the most positive to the most negative. Also, you will compare your experimental voltages with calculated voltages that you obtain from standard reduction potentials. Whenever laboratory conditions differ from standard conditions—you will use 0.1 *M* solutions at room temperature instead of the standard 1.0 *M* solutions at 25°C—the Nernst equation

$$E = E° - \frac{RT}{nF} \ln Q$$

tells how the expected voltage will differ (or will *not* differ, as the case may be) from the standard voltage. Here *E* is the expected voltage, E^o, the standard voltage, *R*, the gas constant or 8.314 J/mol·K, *T*, the absolute temperature, *n*, the number electrons involved in the half-reaction (which equals 2 in each of these cells), *F*, the Faraday constant or 96487 J/volt·mol, and *Q*, the reaction quotient (which takes the same products-over-reactants form as the equilibrium constant). *E* will equal E^o only when *T* equals 0 or *Q* equals 1.

In the second part of the experiment, you will observe the chemical reactivities of these metals and their ions with each other, and arrange the equations for their half-reactions in order of the relative strengths of oxidizing and reducing agents.

Finally, you will compare the results of your electrochemical and reactivity observations.

PROCEDURE

A. Electrochemical Cells

1. Wait until one of the electrochemical cell set-ups (located in the fume hoods) is free. (While you are waiting, you can either stand in line or proceed with part B, as you wish.) When it is your turn, observe that the apparatus consists of four half-cells: Zn*(s)* in 0.1 *M* Zn^{2+}, Cu*(s)* in 0.1 *M* Cu^{2+}, Mg*(s)* in 0.1 *M* Mg^{2+}, and Fe*(s)* in 0.1 *M* Fe^{2+}. Each tube is fitted at the bottom with an ion-permeable membrane and is immersed in a common electrolyte, 0.1 *M* $Na_2SO_4(aq)$. Connecting the metals of any two half-cells creates a voltage between them. Use the voltmeter to measure the voltages of all six possible pairs of half-cells. (You may have to reverse the connections in some cases so that a positive voltage is displayed.)

2. When the voltmeter displays a (positive) voltage, it means electrons are tending to flow into the meter's negative (black) terminal and out of its positive (red) terminal. From this fact,

identify and label the anode and the cathode in each of the six cells.

3. For each cell, write the two half reactions and the overall cell reaction.

4. Arbitrarily set the Zn^{2+}/Zn reduction half-cell potential equal to zero. Then calculate the relative potentials for each of the other metal ions from the cell potentials of the first three cells in steps 1-3 on the report sheet.

5. Using these half-cell potentials, calculate the expected cell potentials of the next three cells in steps 1-3 on the report sheet. Compare these values to the measured values and calculate the percent error.

6. Rank these half-cell potentials from most positive to the least positive.

B. Reactivity of Four Metals

7. Place a tiny sample of zinc, copper, magnesium, and iron in separate small test tubes, appropriately labeled. Add about 2 mL of 0.1 *M* copper(II) sulfate to each. Observe the surface of each metal to see if a reaction is taking place. If a reaction is not immediately obvious, let the mixture stand for several minutes, and check it again. In the table on the report sheet, give a one- or two-word description of each reaction that you observe. Otherwise, place *N. R.* in the box to stand for "No Reaction".

8. Pour off the solution in each test tube, saving the sample of metal in each. Replace any metal sample that became discolored by the previous reaction. Rinse the remaining samples with about 1 mL of distilled water from your squeeze bottle, and discard the rinse water. Now add about 2 mL of 0.1 *M* magnesium sulfate to each test tube. Record your observations.

9. Repeat, using 0.1 *M* zinc sulfate.

10. Repeat, using freshly prepared solution of saturated iron(II) sulfate. (If the solution is not ready-made from the stock room, dissolve 0.8 g of $FeSO_4 7H_2O$*(s)* in 5 mL of distilled water.)

11. Write net-ionic equations for each reaction. Circle the oxidizing agent and underline the reducing agent in each reaction.

12. Rank the metal ions by their strengths as oxidizing agents. The strongest oxidizing agent is the one you observed acting as such in the most reactions. Write the half reaction for the reduction of that ion at the far left of the list. Write the reduction half reaction for the next strongest oxidizing agent, and so on. The weakest oxidizing agent is the ion that did not react with anything; write its reduction half reaction at the far right. Compare the results of Steps 5 and 11. Did the four metal ions come out in the same order? Why or why not?

C. Reactivity of the Halogens

13. Place ½ mL hexane (C_6H_{14}) in each of three small test tubes. Place 1 mL Cl_2(*aq*)—known as "chlorine water" in one test tube, 1 mL Br_2(*aq*)—"bromine water"—in another, and 1 mL I_2(*aq*)—"iodine water—in the third. The nonpolar halogens are more soluble in the nonpolar hexane than in the water, and will be extracted from the water into the hexane. Note the color of the halogens dissolved in hexane. the hexane layer is at the top of each tube, since hexane is less dense than water. *Dispose of hexane in the "waste organic" jug.* ["Chlorine water" is created by adding ~½ mL 1 M HCl(aq) and ~½ mL bleach to the test tube already containing hexane.]

14. Place ½ mL hexane in a small test tube. Add ½ mL of iodide (I^-) solution and then ½ mL of chlorine water (created by adding HCl and bleach). Observe the color of the hexane layer to determine if chlorine (Cl_2) or iodine (I_2) is present in the hexane layer. This should tell you if a reaction has taken place.

Repeat this same process for each of the combinations that are listed in the table below (Page 5) for Step 14, determining if a reaction takes place for each combination. Reactions occur in only three of the six test tubes.

15. Write net ionic equations for the reactions that occurred.

16. Rank the relative reactivity of the three halogens.

8 Oxidation and Reduction

Name ______________________________
Section __________________Locker ____
Instructor ___________________________

Electrochemical Cells

1-3. From your measurements, fill in or circle on each of the following diagrams: the cell voltage, the anode (**A**), the cathode(**C**), the two half-reactions, and the overall cell reaction.

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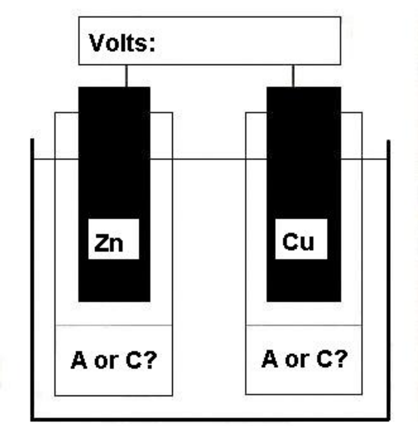
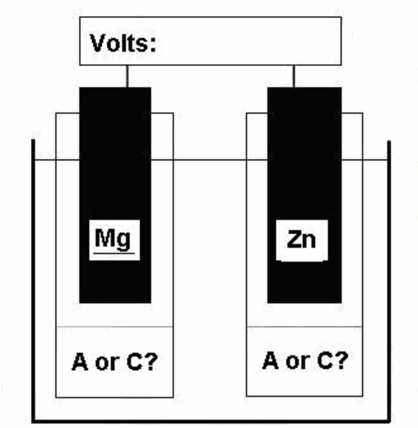
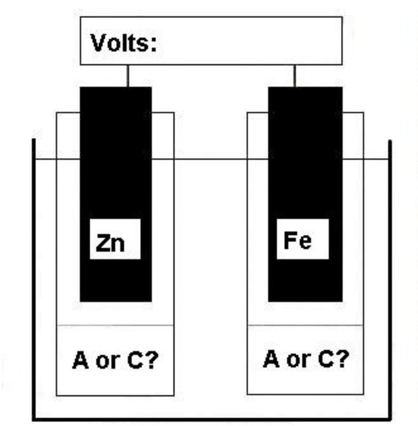
<td></td>
<td></td>
<td></td>
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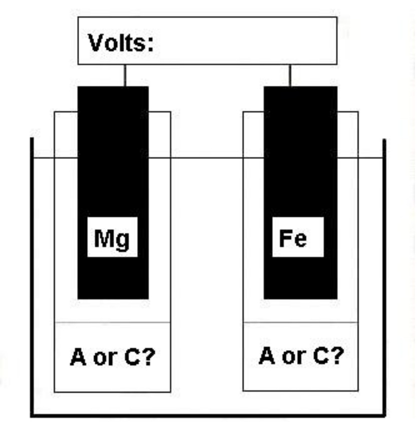
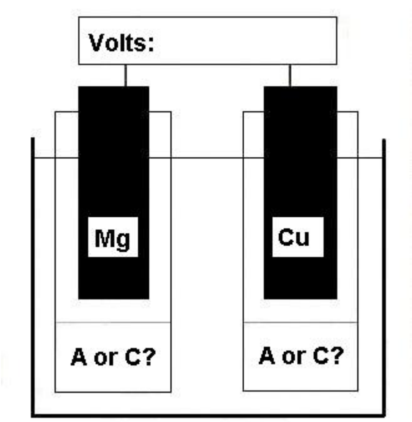
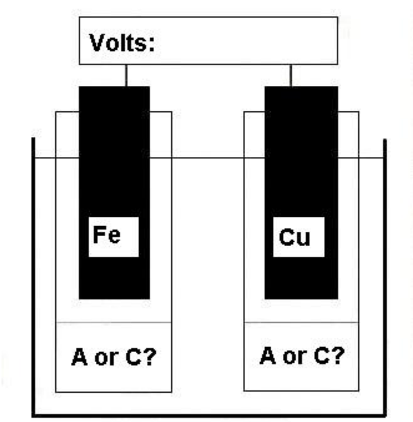
<td></td>
<td></td>
<td></td>
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<tr><td>Cell rxn:</td><td>Cell rxn:</td><td>Cell rxn:</td></tr>
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4. Fill in the relative half-cell reduction potentials from your calculations.

Zn^{2+}/Zn:	Cu^{2+}/Cu:	Mg^{2+}/Mg:	Fe^{2+}/Fe:

CALCULATIONS:

5. Calculate the expected cell potentials for the following cells from the above half-cell potentials. Compare them with your measured values, and determine the percent error. Assume that the expected potential is the accepted value.

Cell	Expected Potential	Measured potential (Part A)	Percent error
$Mg\|Mg^{2+}\|\|Cu^{2+}\|Cu$			
$Fe\|Fe^{2+}\|\|Cu^{2+}\|Cu$			
$Mg\|Mg^{2+}\|\|Fe^{2+}\|Fe$			

CALCULATIONS:

6. Rank the reduction half-cell potentials of the metal ions:

Most positive			Least positive

B. Reactivity of Four Metals

7-10. Fill in the following table with a one- or two-word description of each reaction you observe. Otherwise, enter ***N.R.***

		Zn*(s)*	Cu*(s)*	Mg*(s)*	Fe*(s)*
0.1 *M* $CuSO_4$*(aq)*	Cu^{2+}				
0.1 *M* $MgSO_4$*(aq)*	Mg^{2+}				
0.1 *M* $ZnSO_4$*(aq)*	Zn^{2+}				
sat'd $FeSO_4$*(aq)*	Fe^{2+}				

11. Write the net ionic equations for each reaction that you observed. Circle the oxidizing agent and underline the reducing agent.

12. Rank the reactivities of the metal ions:

Strongest oxidizing agent Weakest oxidizing agent

In Steps 6 and 12, did the four metal ions come out in the same order? Why or why not?

C. Reactivity of the Halogens

	Cl_2	Br_2	I_2
13. Colors in hexane			

14.	Color of hexane layer	Reaction?
Cl_2(*aq*) + I^-(*aq*)		
Cl_2(*aq*) + Br^-(*aq*)		
Br_2(*aq*) + I^-(*aq*)		
Br_2(*aq*) + Cl^-(*aq*)		
I_2(*aq*) + Cl^-(*aq*)		
I_2(*aq*) + Br^-(*aq*)		

15. Write net ionic equations for the three reactions that occurred.

16. Rank the reactivities of the three halogens Cl_2, Br_2, and I_2.

Strongest oxidizing agent				Weakest oxidizing agent

APPLICATION OF PRINCIPLES

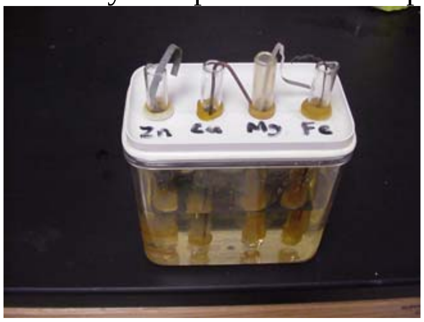
1. The standard reduction potential for the Ag+/Ag half-cell is 0.7994 volts. In each of the following, tell which of the two situations would produce a chemical reaction. Justify each answer with a calculation. Use standard potentials from the text, not the ones you invented for this experiment.

a. Ag*(s)* placed in a solution containing Cu^{2+}, or Cu*(s)* placed in a solution containing Ag^{+}.

b. Ag*(s)* placed in a solution containing Mg^{2+}, or Mg*(s)* placed in a solution containing Ag^{+}.

2. What is the purpose of the ion-permeable membrane and the sodium sulfate electrolyte in the electrochemical cell apparatus?

Laboratory set-up for stockroom personnel.



<u>Electrochemical Cell</u>
Zn(*s*) in 0.1 M $ZnSO_4$(*aq*)
Cu(*s*) in 0.1 M $CuSO_4$(*aq*)
Mg(*s*) in 0.1 M $MgSO_4$(*aq*)
Fe(*s*) in 0.1 M $FeSO_4$(*aq*)

Bath with 0.1 M Na_2SO_4(*aq*)

<u>Dropper bottles</u>
$CuSO_4$(*aq*) & Cu(*s*)
$ZnSO_4$(*aq*) & Zn(*s*)
$MgSO_4$(*aq*) & Mg(*s*)
$FeSO_4$(*aq*) & Fe(*s*)

<u>Dropper bottles</u> (in hood)
HCl(aq) & bleach (for chlorine water)
bromine water
iodine water

Cl^-(*aq*), Br^-(*aq*), I^-(*aq*) solutions