Experiment 6C

ELECTROCHEMICAL ACTIVITY SERIES

MATERIALS: Four 18x150 mm test tubes; one 13x100 mm test tube; test tube rack; 50 mL beaker; 250 mL beaker; 3 mL plastic Pasteur pipet; forceps; marking pencil; samples of Ca, Na, Cu, Zn, Fe, Mg; 6 M HCl; 6 M NH_3; 0.25 M solns. of $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Fe(NH_4)(SO_4)_2$, $Mg(NO_3)_2$; phenolphthalein; saturated Br_2 water; wooden splints, pneumatic troughs.

PURPOSE: The purpose of this experiment is to experimentally rank the electrochemical reactivity of the following elements: Ca, Na, Cu, Zn, Fe, Mg, H_2, and Br_2.

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. Be able to define the following terms: oxidation, reduction, oxidizing agent, reducing agent, electrochemical activity series, and redox couple.

DISCUSSION:

Elements, both metallic and nonmetallic, vary in their tendencies to undergo reactions (reactivity). 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 to form cations, while nonmetals tend to form anions by gaining electrons. The loss of electrons is known as *oxidation*, and when a species gains electrons, it is a *reduction* process. 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. The object of this experiment is to compare the behavior of several metals in oxidation processes, and to use the data collected to create a list of metals in decreasing order of reactivity. Such a table is called an "activity series" and it can be used to predict reactions in many electrochemical processes.

Several experimental tests will be used to determine the relative reactivity of metals. One such test is the reaction of a metal with water, generating H_2 gas.

$$2\,K\,(s) + 2\,H_2O\,(l) \rightarrow 2\,KOH\,(aq) + H_2\,(g)$$

Highly active metals such as potassium react with water very readily. Less active metals do not react readily with water, but may react with acids, to generate hydrogen gas. Such distinctions are a measure of the relative tendency of the metal to lose electrons in this redox process. For example, consider the reaction of cadmium with hydrochloric acid, which is shown in the molecular and net ionic equations:

$$Cd\,(s) + 2\,HCl\,(aq) \rightarrow CdCl_2\,(aq) + H_2\,(g)$$
$$Cd\,(s) + 2\,H^+\,(aq) \rightarrow Cd^{2+}\,(aq) + H_2(g)$$

Compared to metals such as potassium that react with cold water to produce hydrogen, metals such as cadmium that require the acid solutions to react are less active (less easily oxidized), and appear lower on the activity series.

The evolution of hydrogen in the reactions above is a special case of a more general phenomenon - one element displacing (pushing out) another element from a compound in a redox reaction. In the case of the metal-acid reaction, the metal displaces hydrogen from the acid. Experimental evidence indicates that the reaction occurs from left to right, as shown above. The reverse reaction is not favored as hydrogen does not displace cadmium from

cadmium chloride. Therefore, the metal must be more reactive than hydrogen, H_2 (g). Similarly, the relative reactivity of two metals can also be established by observing a reaction between one of the metals and a dissolved cation of the other metal. For example:

$$Cd\ (s) + 2\ AgNO_3\ (aq) \rightarrow 2\ Ag\ (s) + Cd(NO_3)_2\ (aq)$$

$$Cd\ (s) + 2\ Ag^+\ (aq) \rightarrow 2\ Ag\ (s) + Cd^{2+}\ (aq)$$

These redox reactions are sometimes called "single displacement" reactions. The more active element undergoes oxidation, losing its electrons to the other metal ion. The half-reactions for these processes are:

$$Cd\ (s) \rightarrow Cd^{2+}\ (aq) + 2\ e^- \qquad \text{oxidation}$$

$$2\ Ag^+\ (aq) + 2\ e^- \rightarrow 2\ Ag\ (s) \qquad \text{reduction}$$

In this example, since cadmium causes silver ion to gain electrons, cadmium is called the *reducing agent*. (A *reducing agent* causes something else to be reduced and is itself *oxidized*.) The silver ion is reduced to form the neutral metal atom, so Ag^+ 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. If the examples discussed thus far are written in terms of the oxidation step, the series includes:

	Reduced form → Oxidized form + Electrons	
Best	$K \rightarrow K^+ + 1\ e^-$	Worst
	$H_2 + 2\ OH^- \rightarrow 2\ H_2O + 2\ e^-$ (H_2, basic)	
Reducing Agents	$Cd \rightarrow Cd^{2+} + 2\ e^-$	**Oxidizing Agents**
	$H_2 \rightarrow 2\ H^+ + 2\ e^-$ (H_2, acidic)	
Worst	$Ag \rightarrow Ag^+ + e^-$	Best

The reduced form (*e.g.*, K) and oxidized form (K^+) of a given element comprise a pair of chemical species called a redox couple (K/K^+). Note that hydrogen appears in two redox couples, for two different reaction conditions. In basic solutions, symbolized as (H_2 ,basic), the couple is $H_2/OH^-/H_2O$. In acidic solutions, symbolized as (H_2, acidic), the couple is H_2/H^+. These hydrogen oxidation couples are the **reverse** of the reduction reactions observed for water and acid, respectively.

Metals at the top of the list (e.g., K) can be oxidized most easily. Because they are easily oxidized, they are good reducing agents. The elements at the bottom of the list such as silver, Ag, do not readily undergo oxidation, so they are poor reducing agents. However, the oxidized form (Ag^+) from that redox couple will readily <u>gain</u> electrons (*i.e.* undergo reduction), and so it 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 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.

PROCEDURE

Part A. Instructor Demonstrations (Perform in fume hood.)

1. Fill a 600 mL beaker with water and add a few drops of phenolphthalein indicator solution. Invert a water-filled test tube in the beaker, taking care to avoid air bubbles. Clean the surface of a pea-sized piece of calcium metal by scraping it or by briefly dipping it into a dilute acid solution. Carefully drop the clean metal into the beaker, and observe the reaction.

2. Collect the gas and test it with a burning splint. Record the observations in the DATA SECTION.

3. Repeat the demonstration, using a small piece of Na metal. Do not collect the gas evolved from this sample. (In this case, cleaning is unnecessary. A fresh Na surface can be obtained by simply cutting the metal with a spatula).

4. Record the observations in the DATA SECTION.

5. To a test tube containing small pieces of copper metal turnings, add about 5 mL of saturated aqueous bromine solution. Stopper and shake thoroughly. Remove the stopper and heat gently to drive off any elemental bromine remaining.

6. Add 6 M ammonia with a dropper. The deep blue color of $Cu(NH_3)_4^{2+}$ provides a positive indication of the presence of Cu^{2+} ions.

7. Record the observations in the DATA SECTION.

Student Sections

Part B. Reactions of Metals with Water

1. Label the locations of four large tubes in a test tube rack to indicate the metals copper, zinc, iron and magnesium. Place a <u>SMALL</u> sample of the appropriate metal in the corresponding tube.

2. Add about 3 mL of distilled water (1 full plastic pipet) to each of the test tubes. 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. Record your observations in the appropriate table in the DATA SECTION.

Part C. Reactions of Metals with Acid

1. Using the pneumatic trough, decant the water from the test tubes used above. Shake out the metal samples and the last drops of liquid. Remove any metal samples from the funnel using forceps and place them on a paper towel. Prepare a new series of test tubes as above. Reuse metal samples that showed no evidence of reaction and obtain fresh samples of the metals which did react in Part B.

2. Label a small beaker and place about 20 mL of 6 M hydrochloric acid solution in it. <u>Carefully</u> add about 3 mL of 6 M hydrochloric acid (1 full plastic pipet) from the beaker to the test tube containing the copper sample. Watch for signs of reaction and record your observations in the table in the DATA SECTION. Repeat the procedure for the zinc, iron and magnesium tubes, again recording your observations in the table in the DATA SECTION.

3. Retain any excess hydrochloric acid in the beaker for later use.

Part D. Reactions of Metals with Metal Ions

1. To complete the ranking of all of the redox couples in the reactivity series, it is necessary to determine which metals react with various metal ions. (See page E6C-2 for more details.) In the DATA SECTION, list the metal + metal ion combinations that must be run to enable a ranking of all of the oxidation reactions.

2. Using the pneumatic trough, decant the acid solutions from Part C, being careful to avoid dropping the metal samples down the drain. Thoroughly rinse the tubes and samples with water, decant, and then shake out the samples as performed previously.

3. Prepare a new series of test tubes containing small samples of zinc, iron and magnesium. For the iron sample, a common nail will be used. First clean it by dipping the nail into 6 M hydrochloric acid. Use tongs to do this, and rinse with water before placing the nail in the test tube. Fill the small test tube with 0.25 M copper(II) nitrate solution; this small tube will serve as a reservoir for copper(II) ion solutions.

4. Add about 3 mL (one full plastic pipet) of copper(II) solution to each of the test tubes containing the appropriate metal samples (as indicated by the data table). Watch for signs of any reaction, such as dissolution, darkening of the metal, gas evolution, color change of the liquid, etc. Record the observations in the appropriate space in the table in the DATA SECTION.

5. Decant the solutions from the reaction test tubes into the 250 mL waste collection beaker and shake out the metal samples onto an open paper towel. Examine the metal samples for changes. Subtle changes are often hard to detect in colored solutions, so they must be examined closely. Record any additional observations if appropriate.

6. Rinse all of the glassware with distilled water and replace the copper(II) solution in the small test tube with 0.25 M zinc(II) nitrate solution; this small tube will serve as a reservoir for zinc(II) ion solutions. Place samples of the appropriate metals (as indicated by the data table) in the reaction tubes. Repeat the tests of steps 4-6, using the zinc(II) ion solution. Record the observations in the table in the DATA SECTION.

7. Decant the solutions from the reaction test tubes into the waste collection beaker, as above, and rinse the glassware with distilled water. Test samples of the appropriate metals with 3 mL volumes of 0.25M iron(III) solution. Record the observations as above, being sure to think about possible reactions. Remember to examine the metal samples <u>outside</u> of the colored solution as well.

8. Repeat the above tests with samples of the appropriate metals once more, this time using 0.25 M magnesium nitrate solution as the reagent. Record all data in the table in the DATA SECTION.

Clean-up.

1. Collect all of the used metal samples and discard them in the trash can.

2. Place all unused hydrochloric acid solutions into the sink.

3. Place all metal waste solutions in the waste container in the hood.

Name _____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 6C

Part A. Instructor Demonstrations (Perform in fume hood.)

Observations for the reactions of calcium and sodium with water:

Observations for the reactions of copper with bromine:

Part B. Reactions of Metals with Water

METAL	REACTION (Y/N)	OBSERVATIONS
Cu		
Zn		
Fe		
Mg		

Part C. Reactions of Metals with Acid

METAL	REACTION (Y/N)	OBSERVATIONS
Cu		
Zn		
Fe		
Mg		

Part D. Reactions of Metals with Metal Ions

List the metal and metal ion reactions to be studied:

_____

_____

_____

OBSERVATIONS

Metal	Cu^{2+}	Zn^{2+}	Fe^{3+}	Mg^{2+}
Cu				
Zn				
Fe				
Mg				

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DATA TREATMENT
Experiment 6C

Part A. Instructor Demonstrations

(A.1) What gas was evolved in the demonstrations involving sodium and calcium?

(A.2) Based on these demonstrations, write the balanced chemical equations for Ca reacting with H_2O and Na reacting with H_2O. Circle the species that are oxidized in the forward reaction. Put a box around the species oxidized if the reverse reaction were to occur.

_____

_____

(A.3) Write the equation for the redox reaction between copper and bromine(aq). Circle the species that are oxidized in the forward reaction. Put a box around the species oxidized if the reverse reaction were to occur.

$Cu\ (s) + Br_2\ (aq)$ 6 _____

Part B. Reactions of Metals with Water

(B.1) Which of the four metal samples (Cu, Zn, Fe, Mg) reacted with water?

(B.2) Write the net ionic equation for the redox reaction between magnesium and water. The conditions used in this part of the experiment correspond to the (H_2, basic) conditions discussed on page 2. Circle the species that are oxidized in the forward reaction. Put a box around the species oxidized if the reverse reaction were to occur.

$Mg\ (s) + H_2O\ (l)$ 6 _____

Part C. Reactions of Metals with Acid

(C.1) Which of the four metal samples (Cu, Zn, Fe, Mg) reacted with acid?

(C.2) Write the net ionic equation for the redox reaction between one of the metals listed in (C.1) and H^+ (aq). Circle the species that are oxidized in the forward reaction. Put a box around the species oxidized if the reverse reaction were to occur.

_____ (s) + H^+ (aq) 6 _____

(C.3) Using the observations from Parts A, B and C, and the table and discussion on E6C-2, fill in the blanks in the following activity series ranking, for Ca, Na, Cu, Zn, Fe, Mg, (H_2, acidic) and (H_2, basic), and Br^- (aq). To say that a metal is more reactive than (H_2, acidic) means that the metal reacts with aqueous acid to form hydrogen gas. Saying that a metal is more reactive than (H_2,basic) means that the metal reacts with water to form hydrogen gas.

(More reactive)_____(H_2, basic)_____(H_2, acidic)_____(Less reactive)

Note that you now have three groups of reducing agents ranked relative to (H_2, basic) and (H_2, acidic), but you do not have enough information to rank the activity of the metals within each group.

Part D. Reactions of Metals with Metal Ions

(D.1) Select any two metals more reactive than (H_2, basic) and write the oxidation reaction for each in the form found in the table on page E6C-2.

(D.2) 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 D to determine which of the two is higher and which is lower in the series.

Higher: _____

Lower: _____

(D.3) Using the information from **all** of the observations for Parts A, B, C and D, list the oxidation reactions for Na, Br^{6}, Cu, Zn, Fe, Mg, Ca, (H_2,basic) and (H_2, acidic) in order of **decreasing** reactivity. This listing is called an ***activity series***.

most active _____

_____

_____

_____

_____

_____

_____

_____

_____

least active _____

Questions:

1. Use the activity series developed on p. E6C-8 to predict the products in the following. Note that "No Reaction" is a possible answer.

$Zn\ (s) + Ca(NO_3)_2\ (aq)$ 6

$Zn\ (s) + Br_2\ (aq)$ 6

$H_2\ (g) + CuSO_4\ (aq)$ 6

Name _____ Section _____

Date_____

Prelab Exercises
Experiment 6C

1. Write balanced oxidation reactions for the following redox couples. These are the reactions that will be studied in this experiment.

   a. Ca/Ca^{2+}

   b. Na/Na^{+}

   c. Cu/Cu^{2+}

   d. Zn/Zn^{2+}

   e. Fe/Fe^{3+}

   f. Mg/Mg^{2+}

   g. H_2/H^{+}

   h. Br^{-}/Br_2.

2. Carry out the exercises in ChemSkill Builder section 5.6.