Redox Reactions

PURPOSE

To determine relative oxidizing and reducing strengths of a series of metals and ions.

GOALS

- To explore the relative oxidizing and reducing strengths of different metals.
- To gain practice working with electrochemical cells.
- To use experimentally determined cell potentials to rank reduction half-reactions.

INTRODUCTION

The movement or transfer of electrons is central to our understanding of chemical reactions. The study of the transfer of electrons from one reactant to another is the study of **electrochemistry**[1]. Electrons can move spontaneously from higher energy levels to lower energy levels within an atom. A similar movement can take place between two different chemical reactants. If there are electrons in one reactant that are at higher energy than unfilled orbitals of the other reactant, the high energy electrons can transfer to the unfilled orbitals at lower energy. This transfer of electrons from one chemical substance to another is known as an **oxidation-reduction (redox)**[2] or **electron transfer reaction.**

Consider the redox reaction (1) and Figure 1 below.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \tag{1}$$

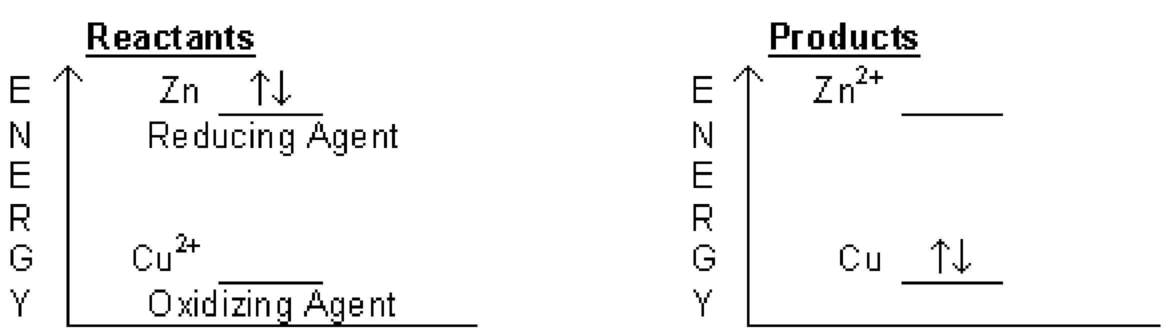

Figure 1: Energy Diagram for Reaction between Zinc Metal and Copper(II) Ion

One reactant, zinc metal, has a pair of electrons at a much higher energy level than an unfilled orbital in the other reactant, copper(II) ion. The electrons in the higher energy orbital in zinc

[1]http://en.wikipedia.org/wiki/Electrochemistry
[2]http://en.wikipedia.org/wiki/Redox

can spontaneously move to the lower energy orbital in copper(II). This electron transfer is a redox reaction.

As the reactant with the high energy electrons "loses" its electrons, its oxidation state increases. In this example, elemental zinc has an oxidation state of 0; loss of two electrons raises its oxidation state to +2. Loss of electrons is an **oxidation** reaction. Conversely, as the reactant with the low energy orbital "gains" electrons, its oxidation state is reduced. Copper(II) has an oxidation state of +2; the elemental metal has an oxidation state of 0. Gain of electrons is a **reduction** reaction.

In a redox reaction, the reactant that loses electrons (is oxidized) causes a reduction and is called a **reducing agent.** In the example above, zinc metal is the reducing agent; it loses two electrons (is oxidized) and becomes Zn^{2+} ion. The reactant that gains electrons (is reduced) causes an oxidation and is called an **oxidizing agent.** Cu^{2+} ion gains two electrons (is reduced) to form copper metal.

In order to have a complete, balanced redox system, there must be at least one reduction and one oxidation; one cannot occur without the other and they will occur simultaneously. For a balanced system, the number of electrons lost in the oxidation reaction must be equal to the number of electrons gained in the reduction step. This is the key to balancing equations for redox reactions. To keep track of electrons, it is convenient to write the oxidation and reduction reactions as **half-reactions**[3]. The half-reactions for Equation 1 are shown below. In this example, zinc loses two electrons and copper(II) accepts both.

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\ \mathrm{e}^- \text{(oxidation half-reaction, reducing agent)} \tag{2}$$

$$\mathrm{Cu}^{2+} + 2\ \mathrm{e}^- \rightarrow \mathrm{Cu} \text{ (reduction half reaction, oxidizing agent)} \tag{3}$$

In a (slightly) more complicated example, copper metal transfers electrons to silver ions, which have an oxidation state of +1. The half-reactions and the balanced net equation are shown below. Since the number of electrons lost must equal the number of electrons gained, two silver ions each accept one electron from a single copper atom, which loses two electrons.

$$\mathrm{Cu} \rightarrow \mathrm{Cu}^{2+} + 2\ \mathrm{e}^- \text{(oxidation half-reaction)} \tag{4}$$

$$\mathrm{Ag}^+ + 1\ \mathrm{e}^- \rightarrow \mathrm{Ag} \text{ (reduction half-reaction)} \tag{5}$$

$$2\ \mathrm{Ag}^+ + \mathrm{Cu} \rightarrow 2\ \mathrm{Ag} + \mathrm{Cu}^{2+} \text{(net reaction)} \tag{6}$$

In this example, copper donates electrons (is oxidized). This indicates that silver ion has a vacant orbital at lower energy than that in which two of copper's electrons reside.

In redox reactions, the oxidized and reduced forms of each reactant are called a **redox couple.** Redox couples are written "ox/red". The oxidized form of the couple is shown on the left, the

[3] http://en.wikipedia.org/wiki/Half-reaction

reduced form on the right with a slash in between. For example, Cu^{2+}/Cu and Zn^{2+}/Zn.

Part A: Relative Reactivities

In Part A of this experiment, you will rank the relative strengths of oxidizing and reducing agents by observing if reactions occur or not. A visible change will accompany each reaction. A solid or gas will form, or a color change will occur. This indicates that the unfilled orbitals in the oxidizing agent are at lower energy than the filled orbitals of the reducing agent. The reaction is the result of electron transfer. If no such change is observed, no reaction has occurred.

You will test three oxidizing agents, Cu^{2+}, Mg^{2+}, and MnO_4^-, to determine their relative reactivities. The solutions that will supply these ions are $Cu(NO_3)_2$, $Mg(NO_3)_2$, and $KMnO_4$, respectively. The reduction half-reaction for each oxidizing agent is shown below in alphabetical order.

$$\mathrm{Cu}^{2+}(aq) + 2\ \mathrm{e}^- \rightleftharpoons \mathrm{Cu}(s) \tag{7}$$

$$\mathrm{Mg}^{2+}(aq) + 2\ \mathrm{e}^- \rightleftharpoons \mathrm{Mg}(s) \tag{8}$$

$$\mathrm{MnO}_4^-(aq) + 8\ \mathrm{H}^+(aq) + 5\ \mathrm{e}^- \rightleftharpoons \mathrm{Mn}^{2+}(aq) + 4\ \mathrm{H_2O}(l) \tag{9}$$

You will react each of them with two compounds that may act as reducing agents, hydrogen peroxide (H_2O_2) and potassium iodide (KI).

You will then test three reducing agents, Cu(s), Mg(s), and Zn(s) to determine their relative reactivities. The oxidation half-reaction for each reducing agent is listed below in alphabetical order.

$$\mathrm{Cu}(s) \rightleftharpoons \mathrm{Cu}^{2+}(aq) + 2\ \mathrm{e}^- \tag{10}$$

$$\mathrm{Mg}(s) \rightleftharpoons \mathrm{Mg}^{2+}(aq) + 2\ \mathrm{e}^- \tag{11}$$

$$\mathrm{Zn}(s) \rightleftharpoons \mathrm{Zn}^{2+}(aq) + 2\ \mathrm{e}^- \tag{12}$$

You will react each of them with two species that may act as oxidizing agents, water (H_2O) and hydronium ion (H_3O^+) supplied by hydrochloric acid.

Note that the Cu^{2+}/Cu couple and the Zn^{2+}/Zn couple are also examined in Part B of this experiment. Be prepared to compare the relative reactivities from Part A with your observations from measuring cell potentials in Part B.

Part B: Half-Cell Potentials

When electrons are transferred spontaneously (downhill in free energy), they can do work in an external circuit if the half-reactions are separated into different compartments. This is how batteries work. Such devices are called **galvanic cells**[4]. It is also possible to set up an **electrolytic cell**[5], in which an external voltage (energy source) is used to drive a redox reaction in the nonspontaneous direction. Many industrial processes involve electrolysis. An important example is the production of aluminum metal from its ore (Al_2O_3).

Separating half-reactions also allows one to measure the energy difference between the electrons in the **donor orbitals** of a reducing agent and the **acceptor orbitals** of an oxidizing agent. You will combine a series of redox couples and measure the energy differences between them. This is typically performed in an electrochemical cell. One is shown in Figure 2 below.

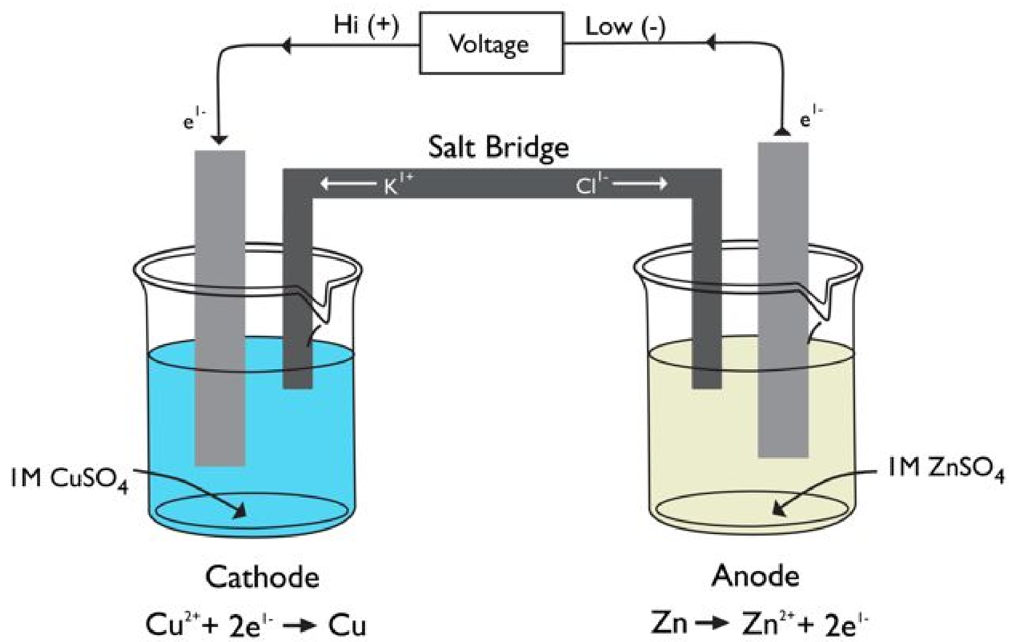

Figure 2: Electrochemical Cell for the Reaction between Copper Metal and Zinc Ion

In a galvanic cell, the half-cells are vessels that contain a strip of the metal in a solution of the corresponding metal ion. The metal strips are called **electrodes**[6]. The electrode at which reduction occurs is called the **cathode**[7] and the electrode at which oxidation takes place is called the **anode**[8].

Connecting the electrodes through a load forms the external circuit. As in the illustration, the load will be a voltmeter. The electrons will travel from the high energy orbitals in the reducing agent at the anode, through the external circuit, to the lower energy orbitals in the oxidizing agent at the cathode. To complete the circuit, a **salt bridge**[9], which allows ions to travel from one half-cell to the other, is used to connect the two half-cells.

[4] http://en.wikipedia.org/wiki/Galvanic_cell
[5] http://en.wikipedia.org/wiki/Electrolytic_cell
[6] http://en.wikipedia.org/wiki/Electrode
[7] http://en.wikipedia.org/wiki/Cathode
[8] http://en.wikipedia.org/wiki/Anode
[9] http://en.wikipedia.org/wiki/Salt_bridge

When a voltmeter is used as the load, the potential difference between the oxidizing and reducing agent can be measured. The first potential difference you will measure will be between the Cu^{2+}/Cu couple and the Ag^{+}/Ag couple. You will use this to set up your voltmeter so a positive reading is obtained. Recall from Equations 4–6 that copper metal donates electrons to silver ions. Copper metal is oxidized in this reaction, so the Cu^{2+}/Cu couple is the anode. Silver ion is reduced, so the Ag^{+}/Ag couple is the cathode. Electrons travel toward the cathode, the more electrically positive electrode, in a spontaneous reaction. The potential difference, E_{cell}, is defined as

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}. \tag{13}$$

In a galvanic cell, the cell potential must be positive if the cathode and anode are properly identified.

You will then measure the potential difference between the Cu^{2+}/Cu couple and several other redox couples consisting of metals and their ions. One of the couples will be Zn^{2+}/Zn. From Equations 1–3, we know that copper(II) is reduced in this reaction, so the Cu^{2+}/Cu couple is the cathode. However, when the Cu^{2+}/Cu couple is connected to the Ag^{1+}/Ag couple, the Cu^{2+}/Cu couple is the anode. What effect will this have on the measurement? If the Cu^{2+}/Cu couple is maintained at the same terminal of the voltmeter for all the measurements, those in which it is the cathode will show negative potentials. This simply indicates that electrons are traveling through the voltmeter in the opposite direction from what was measured in the cell with the Ag^{+}/Ag couple. Voltmeters are sensitive to the direction of electron flow (electrical current), and indicate the direction by means of the sign on the potential difference.

Therefore, with this experimental set-up, a positive voltage means that the Cu^{2+}/Cu couple is the anode, and a negative voltage means that the Cu^{2+}/Cu couple is the cathode. Thus, you should obtain a series of potential differences that can be arranged from most negative to most positive. This order will tell you the energy relationships between filled orbitals in the metals and vacant orbitals in the ions. The couple that produces the most negative potential difference with copper will have the metal with the highest energy electrons. It will be the strongest reducing agent. The couple that produces the most positive potential difference with copper will have the lowest energy unfilled orbitals. It will be the strongest oxidizing agent.

For Part B, you will use a simple version of an electrochemical cell. It will consist of a round plastic base with one center indentation lined with a porous frit which contains the salt bridge solution and indentations around the circumference for the various half-cell solutions. The metal electrodes are wires that will be placed into the solutions containing metal ions. When the leads of the voltmeter are connected to the two metal electrodes, the potential difference between the two cells will be measured just as in Figure 2 above.

EQUIPMENT

Part A: Relative Reactivities

1 ceramic spot plate

3 30 mL beakers

1 deionized water squirt bottle

Part B: Half-Cell Potentials

1 MicroLab Multi-EChem Half Cell module

1 MicroLab interface

1 voltmeter alligator clip lead

REAGENTS

Part A: Relative Reactivities

~6 drops 0.1 M $Cu(NO_3)_2$

~6 drops 0.1 M $Mg(NO_3)_2$

~6 drops 0.1 M $KMnO_4$ (acidic)

~9 drops 3% H_2O_2 solution

~9 drops 0.1 M KI

~9 drops phenolphthalein solution

~2 pieces Cu metal

~2 pieces Zn metal

~2 pieces Mg metal

~20 mL 3 M HCl

~30 mL tap water

Part B: Half-Cell Potentials

0.1 M $Cu(NO_3)_2$

0.1 M $AgNO_3$

0.1 M $Pb(NO_3)_2$

0.1 M $Zn(NO_3)_2$

0.1 M KNO_3

2 × ~1.5" copper wire

~1.5" silver wire

~1.5" lead wire

~1.5" zinc wire

SAFETY

The potassium permanganate solution ($KMnO_4$) is a strong oxidizing agent; it is also acidic and corrosive. The solution of 3M HCl is acidic and corrosive. Both solutions can attack the skin and cause permanent damage to the eyes. If either of these solutions splashes into your eyes, use the eyewash immediately. Hold your eyes open and flush with water. If contact with skin or clothing occurs, flush the affected area with water. Have your lab partner notify your instructor about the spill.

3M HCl gives off acidic and irritating vapors. Add it carefully to your beakers in the fume hood on the side shelf. Avoid inhaling the vapors.

The reducing agents produce hydrogen gas when exposed to water and/or acid. Keep the reactions away from ignition sources, and rinse acid off metal before discarding it. Do not tightly cap the waste container.

As with all labs, be sure to wash your hands thoroughly after handling any chemicals and avoid touching your eyes and mouth during lab.

WASTE DISPOSAL

The solutions from Part A1 of the experiment should be rinsed into the waste container for oxidizing agents. There will be a funnel in the container. Pour the contents of the well plate into the funnel, and then rinse the plate with water from a squeeze bottle.

The metals from Part A2 of the experiment should be removed from the reactions with forceps, rinsed with water if they have been exposed to acid, blotted to remove excess water, then discarded in the container for used metals. Do not tightly cap this container; hydrogen gas could build up pressure in it. Liquids from this experiment can be flushed down the sink.

The solutions from Part B of the experiment should be rinsed into the waste container for redox solutions. There will be a funnel in the container. Pour the contents of the well plate into the funnel, and then rinse the plastic base with water from a squeeze bottle. The metal wires should be returned to the set-up sheet to be used by the next lab section.

PRIOR TO CLASS

Please complete WebAssign prelab assignment. Check your WebAssign Account for due dates. Students who do not complete the WebAssign prelab are required to bring and hand in the prelab worksheet.

LAB PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

For this lab, Part A will be set up at your lab station. During the lab period, each pair should take turns going to the side shelf to record measurements for Part B.

Part A1: Ranking Oxidizing Agents

1 Obtain a ceramic well plate.

2 Add 3 drops of $Cu(NO_3)_2$ solution to the first well, 3 drops of $Mg(NO_3)_2$ solution to the second well, and 3 drops of $KMnO_4$ solution to the third well.

3 Add 2 drops of H_2O_2 solution to each well. If something happened, write “R” (reaction) in Data Table A1 and make a brief note of what occurred in the space below it. If nothing happened, write “NR” (no reaction) in the space. Any oxidizing agent that reacted with the H_2O_2 is a stronger oxidizing agent than any which did not.

4 If no reaction was observed, place three drops of the oxidizing agent in another well.

5 Add three drops of KI solution to each well. If something happened, write “R” (reaction) in Data Table A1 and make a brief note of what occurred in the space below it. If nothing happened, write “NR” (no reaction) in the space. Any oxidizing agent that reacted with the KI is a stronger oxidizing agent than any which did not.

6 Pour the contents of the well plate into the waste bottle for oxidizing agents and rinse it with your squirt bottle. The rinsings should also go into the waste bottle.

Pour the contents of the well plate into the waste bottle for oxidizing agents and rinse it with your squirt bottle. The rinsings should also go into the waste bottle.

Part A2: Ranking Reducing Agents

1 Obtain three 30 mL beakers and label them Cu, Mg, and Zn.

2 Add 10–15 mL of tap water to each, then place a small piece of copper metal in the one labeled “Cu”, magnesium metal to the one labeled “Mg” and zinc metal to the one labeled “Zn”.

3 To each beaker, add 3 drops of phenolphthalein indicator. If something happened, write “R” (reaction) in Data Table A2 and make a brief note of what occurred in the space below it. If nothing happened, write “NR” (no reaction) in the space. Any reducing agent that reacted with the water is a stronger reducing agent than any which did not.

4 With the forceps provided by the waste jar, remove the metals from each of the three beakers. If no reaction occurred, rinse the metal with deionized water and place it on a paper towel to dry. This metal can be used in step 5. If a reaction did occur, place the metal in the *Used Metal Jar.* The liquids can be flushed down the sink with water.

5 Rinse and dry the beakers, then place a new sample of the metals that did not react with water in the properly labeled beakers.

6 Add about 10 mL of tap water to each beaker.

7 Go to the side shelf fume hood and add 10 mL of 3 M HCl solution to each beaker. If something happened, write “R” (reaction) in Data Table A2 and make a brief note of what occurred in the space below it. If nothing happened, write “NR” (no reaction) in the space. Any reducing agent that reacted with the acid is a stronger reducing agent than any which did not.

8 With the forceps provided near the waste jar, remove the metals from each of the beakers, rinse them with deionized water from a squeeze bottle and blot them dry. Place them in the *Used Metal Jar.* The liquids can be flushed down the sink with water.

9 Wash and dry all your equipment and return it to the set-up area where you found it.

Part B: Half-Cell Potentials

1 To activate the MicroLab voltmeter, first ensure the MicroLab interface is turned on, as indicated by a green light in the "o" of the MicroLab logo. On the computer desktop, double-click on the MicroLab icon to open the software. A box will appear to choose an experiment. Highlight "Half-cell Meter" and click "OK." Make sure that the voltage input is selected and click "OK." This will bring up the meter display of measured voltage.

2 Fill the center of the cell, shown in Figure 3, with fresh KNO_3 solution.

3 Fill the wells with the metal ion solutions and place the corresponding metal wire in the solution:

Wells 1 and 2: $Cu(NO_3)_2$/Cu. The Cu wire will have a characteristic copper color.

Well 3: $Zn(NO_3)_2$/Zn. The Zn wire will be gray and difficult to bend.

Well 5: $Pb(NO_3)_2$/Pb. The Pb wire will be dull gray and very bendable.

Well 7: $AgNO_3$/Ag. The Ag wire will be shiny and look like silver.

Figure 3: MicroLab Multi-EChem Half Cell module

4 For the Copper-Copper cell, attach the black alligator clip lead to the copper wire in Well 1.

5 Next attach the red alligator clip lead to the other copper wire in Well 2.

6 Measure the potential in volts and record it in Data Table B1. This value should be very close to 0.0 V since there is no potential difference between copper and itself. If you do not find this result, consult your instructor.

7 When you are finished taking your measurement, remove the red lead from the copper wire and attach it to the silver wire. Measure the potential in volts and record it in Data Table B1. The Silver-Copper cell should have a positive cell potential. If it does not, consult your instructor.

8 Repeat step 7 for the Zinc-Copper and Lead-Copper couples.

9 When finished, dispose of all waste in the appropriate container in the hood, rinse the cell, and refill the *center cell* with KNO_3 solution.

10 Enter the four couples into Data Table B2, arranging them in order from most negative potential to most positive potential.

11 We have treated the Cu^{2+}/Cu couple as a reference point for our measurements. However, the standard hydrogen electrode (SHE) is defined by international convention as the zero volt reference. The reduction potential of Cu^{2+}/Cu is +0.34 V relative to this standard. Therefore by adding +0.34 V to each of the potentials you measured vs. Cu^{2+}/Cu will convert them to potentials vs. SHE. Enter these values in Data Table B2, column 3.

12 Refer to the table of Standard Reduction Potentials given on the inside front cover of this lab manual to find the actual standard reduction potentials of these four couples. Enter these values in Data Table B2, column 4.

13 Before leaving, go to a computer in the laboratory and enter your results in the In-Lab assignment. If all results are scored as correct, log out. If not all results are correct, try to find the error or consult with your lab instructor. When all results are correct, note them and log out of WebAssign. The In-Lab assignment must be completed by the end of the lab period. If additional time is required, please consult with your lab instructor.